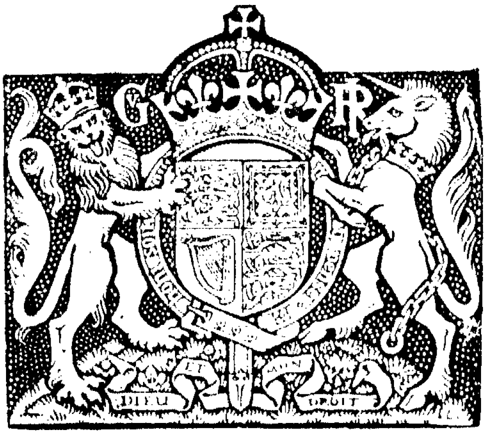

IMPERIAL INSTITUTE
OF
AGRICULTURAL RESEARCH, PUSA.

# PROCEEDINGS

OF THE

# ROYAL SOCIETY OF LONDON

SERIES A

CONTAINING PAPERS OF A MATHEMATICAL AND
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PROCEEDINGS OF

THE ROYAL SOCIETY.

*SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.*

# *Address of the President, Sir Ernest Rutherford, O.M., at the Anniversary Meeting, November 30, 1928.*

During the past year the losses to our Society by death have been unusually heavy, including three Foreign Members, thirteen Fellows, and two Fellows elected under Statute 12, the Earl of Oxford and Asquith and Viscount Haldane. While the main work of Lord Haldane lay in legal and administrative fields, he always had a deep interest in science and its philosophy, and gave much valuable help to the cause of University Education.

The death of Prof. P. H. VON GROTH, Foreign Member of our Society, at the age of 84, removes a notable figure from the Science of Mineralogy. Distinguished as investigator and writer and editor for 39 years of the 'Zeitschrift für Krystallographie und Mineralogie,' he widely influenced the development of his science, and by his own researches and through his students made notable contributions to our knowledge.

The death of HENDRIK ANTOON LORENTZ, Foreign Member of the Royal Society and Nobel Laureate, has deprived physical science of one of the greatest figures of our time. He will be remembered mainly by his extension of Maxwell's electromagnetic theory. He introduced a new precision into this theory, and brought it into line with current experimental physics, by breaking up Maxwell's electric charges into crowds of electrons. Especially noteworthy was his explanation of the newly-discovered Zeeman Effect, in terms of electronic motion inside the atom. Contemporaneously with Larmor, he examined and discussed the effects produced by the motion of an electric system through "the ether." This part of his work culminated in a proof that the effect of this motion could be exactly reproduced by a modification of the measures of time and space in the system. The equations which embody this result, universally known as "Lorentz's transformation," ultimately formed the foundation stone of the Theory of Relativity.

In his latter years, he naturally and by general consent took the leading place in every Continental congress of physicists. Those who have seen him presiding over such functions can never forget his unfailing tact and courtesy, his geniality and kindness to all, his ready wit, his command both of language and languages, and the vast store of scientific knowledge which was ever held in reserve, to be brought into service when needed.

At the request of the Society, I attended the funeral of Lorentz at Haarlem, which was national in scope and testified to the high place he held in the esteem of all sections of his countrymen. Eulogiums on the work and personality of Lorentz were spoken at the graveside by Prof. Ehrenfest, Langevin, Einstein and myself.

By the death of W. H. DINES, at the age of 73, Meteorology has lost an outstanding pioneer in the study of the upper atmosphere. By means of kites and balloons and measuring apparatus of entirely his own design, he was one of the first to make a systematic study of the meteorological state of the upper air. For 20 years Director of Experiments in the Upper Air for the Meteorological Office, he rendered great services to the Science he loved.

Sir AUBREY STRAHAN, who died on March 4th, was till 1920 Director of the Geological Survey of Great Britain and a leading authority on the stratigraphical Geology of this country, and especially on that of the coalfields. He had been President of the Geological Society of London, and a member of the Royal Commission on Coal Supplies. Elected to our Fellowship in 1903, he gave valued service on the Council and Committees of the Society, acting in the last months of his life as Chairman of a Committee appointed to draft a report on Museums and Public Galleries.

In Sir DAVID FERRIER, who has died in his 87th year, we have lost a pioneer investigator of the physiology of the brain, whose work laid the experimental foundation of all modern knowledge of the localised functions of the cerebral cortex, and thereby opened a new epoch in the medical diagnosis of disease or injury of the brain, and in their relief by surgical operation. Ferrier was one of the founders of the Physiological and of the Neurological Society, and one of the small group who, in 1878, started the Journal 'Brain,' to deal with neurology in its widest experimental and clinical aspects. For many years an honoured and successful physician, he preserved to an advanced age an enthusiastic interest in the advance of neurology by the experimental method. In 1906–1908 he was a Vice-President of the Society, of which he had been a Fellow for 52 years at the time of his death.

Science has suffered a severe loss by the early death of THEODORE W. RICHARDS, Director of the Gibbs Memorial Laboratory, Harvard University, Nobel Laureate in Chemistry, Foreign Member of our Society and Davy Medallist. He early devoted himself to the accurate determination of the atomic weights of the elements and introduced many new methods leading to much increased precision in the measurement of these fundamental constants. The value of his work has been universally recognised, and his laboratory at Harvard attracted many research students from all parts of the world. He was much interested in the compressibility of atoms and molecules and made many accurate measurements in this field. A man of wide interests and sympathies, he had many friends in this country.

**Hans Friedrich Gadow**, of German birth, but of British nationality since 1884, was for many years lecturer and reader in the advanced morphology of vertebrates in the University of Cambridge. His researches and writings on vertebrate anatomy, and especially on that of birds, reptiles, and amphibia, have had a great and stimulating influence on zoological thought. A naturalist as well as an anatomist, he sought every opportunity of seeing the forms which he studied under natural conditions, keeping many alive in his garden and wandering as far afield as the caves and mountains of Northern Spain and of Mexico. A man of robust and enthusiastic temperament he is held in grateful memory by many Cambridge men as a popular and influential teacher.

**John Horne**, a former Assistant Director of the Geological Survey of Great Britain, was in charge of the Geological Survey of Scotland from 1901 until 1911. In association with different colleagues he was responsible for important memoirs on the structure of the North-West Scottish Highlands and on the Silurian rocks of Scotland. At the time of his death, at the age of 80 years, he was still engaged in the completion of a work on the Geology of Scotland, begun in collaboration with the late B. N. Peach.

Sir **John Thornycroft**, who died in his 85th year, became a Fellow of the Society in 1893. A pupil at Glasgow of Kelvin and Rankine, he began the construction of small high-speed craft on the Thames almost simultaneously with Sir Alfred Yarrow. In 1877 he built for the Admiralty his first torpedo boat, followed in rapid succession by other craft, including, in 1907, the ocean-going destroyer "The Tartar," driven by Parsons turbines at 35·6 knots. In time his yard was moved to Southampton, and from it during the War was launched a stream of destroyers and flotilla leaders. During his later years he devoted himself to some of the problems which troubled the builder of high-speed vessels, utilising for the purpose a small tank constructed in his grounds.

**Charles Chree**, after graduating in the University of Aberdeen, came to

Cambridge, and was 6th Wrangler in 1883, gaining a Fellowship in King's College in 1885. In 1893 he was appointed Superintendent of the Kew Observatory, and filled this post with much distinction until his retirement in 1925. He published many original papers on subjects connected with terrestrial magnetism and atmospheric electricity and elasticity. Of international reputation, the value of his work was recognised by the award to him of the Hughes Medal of the Society.

Sir HORACE DARWIN, son of Charles Darwin, was educated as an engineer. He will long be remembered as the man who, by the application of engineering principles, transformed the industry of scientific instrument making in this country. Soon after Michael Foster went to Cambridge as teacher in physiology, Darwin began, in partnership with Dew Smith, to make instruments for the new laboratory. The work grew, and in time developed into the Cambridge Scientific Instrument Company, with Darwin as its chairman and inspiring genius. Many of the instruments were of his own design, and practically all bore the impress of his supervision. He was one of the first to apply the principles of geometrical design laid down by Kelvin and Maxwell. The changes in instrument making during the past fifty years have been far reaching. Darwin was a leader in this advance, a friend ever ready to help those who came to him for advice.

DIARMID NOËL PATON, for 22 years Regius Professor of Physiology in the University of Glasgow, was an eminent and successful teacher and an enthusiastic investigator of problems drawn from a wide range of his subject. He was among the earliest of British physiologists to investigate metabolic problems and in more recent years had devoted, with his pupils, many years of experimental study to the function of the parathyroid glands. In an age of increasing specialisation he remained conspicuous for the width of his knowledge and interest in physiology and in its practical application to sociology and medicine.

G. H. BRYAN was an applied mathematician of distinction. His early work lay in the fields of hydrodynamics, thermodynamics and the kinetic theory of gases. Later he turned his attention to the problem of aviation; he was the first to investigate stability of flight by treating the moving aeroplane as a system undergoing small oscillations about a state of steady motion, thus laying the foundations of the theory of stability in aviation.

By the death of Sir CHARLES TOMES, in his 83rd year, the Society has lost from its Fellowship a great pioneer in dental anatomy. In his continuation of the work of his father, also one of our Fellows, he may be said to have founded the science of comparative dental histology. As a member and Treasurer of the General Medical Council, he was largely responsible for raising the standard of scientific training for the practice of dental surgery.

Sir ALEXANDER KENNEDY, who has recently passed from us, had been for over forty years a Fellow of our Society. In 1874 he became Professor of Engineering in University College, Gower Street, and established there the first Engineering Laboratory in this country, devising a method of education which has been followed widely both at home and abroad. He was one of the first to realise the need for placing structural engineering on a sound mechanical basis and was largely responsible for the introduction of testing machines. On resigning his professorship in 1889, he commenced practice as a consulting engineer and in that capacity designed electrical works for power and lighting in many parts of the Empire. He was a man of many interests and, of late years, by his photographic records of the ruins of Petra made known to the world some of the wonders of the civilisation of which it was the centre.

Sir HUGH KERR ANDERSON, Master of Caius College, Cambridge, since 1912, and a Fellow of our Society since 1907, was a member of our Council at the time of his recent death, at the early age of 63. Returning to Cambridge in 1891, on the completion of his medical course in London, he devoted himself during the next 14 years, with self-sacrificing zeal and conspicuous success, to research and teaching in his chosen subject of physiology. He was one of the investigators who were then unravelling the intricacies of the autonomic system and shaping the conceptions of its function now everywhere accepted. The series of classical papers in which he was associated with the late Prof. Langley, and his later and independent work on the complex reactions of the pupil of the eye, had shown him to the world of science as a coming master in his subject; while to every Cambridge man who in that period entered upon research or higher study in physiology, Anderson had been lavish in his gift of interest, encouragement and personal help. From 1905 onwards the recognition of his aptitude for business drew him, always diffident and reluctant, away from research into the wider affairs of his College and of his University. As a member of the Royal and Statutory Commissions, and in many other capacities, he did inestimable service to Cambridge, to science, and to education, and earned the honour and affection of a wide circle beyond his University and our Society.

Turning to other matters, I shall say a few words on events of interest to our Society during the year. After the normal period of office, Sir Richard Glazebrook retires to-day from the position of Foreign Secretary, and I am glad to take this opportunity to convey to him the gratitude of the Society for his valuable services. In a difficult time, he has very efficiently represented our Society at the meetings of the International Research Council and has been indefatigable in his correspondence on international questions. We are fortunate to secure as his successor Sir Henry Lyons, who, in association with Sir Richard Glazebrook, has represented the Society at International meetings. His wide experience in this direction had led to his appointment as Secretary of the International Research Council in succession to Sir Arthur Schuster, who has recently retired from this important office. Since its foundation, he has been General Secretary of the Union for Geophysics.

Before the meeting on June 21, I had the pleasing task of accepting on behalf of the Society a portrait by Mr. R. G. Eves of our former President, Sir Charles Sherrington, which was presented by Sir John Rose Bradford on behalf of the subscribers. The Society is proud to possess this portrait, which is now hanging on our walls, and I think all will agree that it is an excellent likeness of my distinguished predecessor. It will serve as a permanent memento of one whose great and still continued services to Science and our Society we all gratefully recognise.

I have already referred to the loss of that veteran investigator Sir DAVID FERRIER. His friends and admirers have collected a fund of £1,000 which they have presented to the Society for the foundation of a Lecture in his memory. The Society has gratefully accepted this offer, so that in future on the biological side in addition to the well-known Croonian Lecture, there will also be a "David Ferrier Lecture" to be given at intervals and on subjects to be determined later.

It will be remembered that in the year 1922 our Society made a new departure by instituting Royal Society Professorships. With the aid of the Foulerton Fund, bequeathed to the Society, and the munificent gift of Sir Alfred Yarrow, we have been able in the last few years to appoint five professors, two Foulerton Professors in the medical sciences and three Yarrow Professors in the physical sciences. The main object of our Society is the "Improvement of Natural Knowledge" by discovery, and the main line of discovery must depend upon research. The Society has endeavoured to attain this object in two ways, first through its Studentships or Fellowships, six in number, including the Sorby, Foulerton, Mackinnon, Moseley, Tyndall and Armourers' and Brasiers', awarded to younger men who have shown marked promise as investigators, and secondly, through its Professorships, which are awarded to those who have shown over a longer period an unusual original capacity for advancing knowledge by experiment. The holders of these Professorships are expected to devote their whole attention to research and are freed from all duties of routine teaching and administration.

As the Royal Society has no laboratory of its own these Professorships may be held in any scientific institution which is in a position to offer suitable research facilities. A satisfactory feature of this scheme of administration lies in the fact that the Royal Society does not compete with existing institutions, but co-operates with and reinforces them. In all cases so far arrangements have been made for our Professors to continue their work in the same laboratories as before, and we are grateful to the Universities and Institutions concerned for the cordial and generous way in which they have co-operated with the Royal Society for this purpose.

The creation of Research Professorships by the Society was in the nature of an experiment, but I think all will agree that the experiment has proved an unqualified success. We have been fortunate in being able to attract some of our ablest and most original workers, who have devoted themselves to their investigations with zeal and enthusiasm, as evidenced by the high quality of their accomplished work. As it is now six years since the institution of the first professorship it has been thought desirable that I should give a brief review of some of the work carried out by our Professors. This is a difficult task in a limited time, but I hope I shall be forgiven for any shortcomings.

Prof. A. Fowler, who was appointed Yarrow Professor on December 1, 1923, has continued his researches in the Astrophysics Laboratory of the Imperial College of Science and Technology. Everywhere recognised as one of the most skilful of our experimenters in spectroscopy, he has during his tenure of office contributed to our 'Proceedings' a number of important papers, which have widely extended our knowledge of the modes of vibration of atoms under different conditions of excitation, when they have been deprived of one or more of their normal number of electrons.

His attention has been directed mainly to the production and analysis of the spectra of some of the lighter elements at successive stages of ionisation, including carbon, nitrogen, oxygen and silicon. These spectra are not only of importance from the theoretical standpoint, but also in their application to the interpretation of the spectra of the hotter stars. He has obtained data of precision over a wide range of experimental conditions, and covering a range of spectrum from the extreme ultra-violet to the infra-red. The investigation of these spectra has presented considerable experimental difficulty, especially in connection with the elimination of impurities. The results obtained for nitrogen and oxygen have already found an application of special interest, in the use which has been made of them by Bowen in his important interpretation of previously unidentified lines in the spectra of gaseous nebulæ.

During the tenure of his professorship Prof. Fowler has also been charged with the direction of the work of a number of research students and assistants at the Imperial College, some of whom have published valuable papers on spectroscopic subjects.

Prof. G. I. Taylor, who was appointed Yarrow Professor on December 1, 1923, continued his investigations in the Cavendish Laboratory, Cambridge. Prof. Taylor possesses that unusual combination of power of detailed mathematical analysis coupled with an ability to design and carry out difficult experiments. He has been specially interested in studying the modes of deformation of single crystals when subjected to uniform strain. The ordinary engineering tests applied to a specimen of metal merely give the average stress over a large number of crystal grains. The discovery of methods of producing single crystals of metals has made it possible for the first time to know the direction and magnitude of the stress throughout the crystal. Prof. Taylor and his co-workers have now determined the relationship between stress, strain and crystal axes for aluminium, iron and some other metals, with most interesting and important results. This work has been extended by other investigators at home and abroad, and to include cases where the stress is alternating.

I can only refer in passing to his continued interest in problems of hydrodynamics, where he has made calculations leading to predictions concerning fluid motion and the behaviour of bodies immersed in fluids. These have been verified by simple experiments shown before our Society. Recently he has turned his attention to the effect of compressibility on the flow of air past bodies moving at high speeds. This problem is now acquiring great importance in aeronautics owing to the rapidly increasing speed of aircraft, but difficulties of mathematical analysis have so far prevented more than very limited advances towards a dynamical theory. Prof. Taylor has now invented a machine, a kind of mechanical mathematician, by means of which problems of flow can be solved, which have so far defeated ordinary human mathematicians. He is now applying this machine to problems of practical importance in aeronautics.

Prof. O. W. Richardson, who was appointed third Yarrow Professor on August 1, 1924, continued to work in the laboratory of King's College, London. Like Prof. G. I. Taylor, he is equally at home in the theoretical and experimental side of physics. His main work in the last few years has been connected with the elucidation of the complicated spectrum of the hydrogen molecule. While the types of vibration of the hydrogen atom are comparatively simple and well understood, very little progress had been made in deciphering the spectrum of the molecule, which shows several thousand bands. The interpretation of this spectrum, which is obviously of great importance to the study of molecular structure, presents peculiar difficulties. These have been largely overcome, and Prof. Richardson has taken a large part in this successful work. The results have been interpreted in terms of the wave-mechanics, and the values obtained for the moment of inertia of the molecule, its ionisation potential and heat of dissociation, fit in well with other observational data. The peculiar alternating intensity of the band spectra appears to show that the hydrogen nucleus has a moment of momentum, like the electron.

In addition to a number of papers on this subject Prof. Richardson, in collaboration with his research students, has continued his important investigations in thermionics, ionisation potentials and X-rays ; nor must I omit mention of his excursions into the field of theoretical physics, where he has considered the application of the new mechanics to the theory of the extraction of electrons from a cold conductor by an electric field, and, in conjunction with Mr. Flint, to other problems of theoretical interest.

The first Foulerton Professor, the late Prof. E. H. Starling, was appointed in 1922, and I had occasion last year, in recording his death, to refer to his distinguished record of research during his tenure of the chair. The second Foulerton Professor, Dr. Archibald Vivian Hill, was appointed less than three years ago, in January, 1926. Since then he has carried out an important series of investigations on the energy changes and physico-chemical processes involved in the measurable vital activities of muscle and nerve. He has measured, for instance, with specially devised apparatus of extreme delicacy, the minute quantity of heat liberated in the passage of a wave of excitation along a nerve, and also the different factors concerned in the efficient muscular activity of man, as exhibited in the running of trained athletes. It is significant of the wide interest in these researches, to which his Foulerton Professorship has enabled Dr. Hill to devote his whole time, that they have been published, largely in our own 'Proceedings,' under the names of some sixteen investigators, who have come to work with him from seven different countries.

The Council have recently decided to fill the other Foulerton chair, vacant since the death of Prof. Starling, and I am able to make this first announcement of the appointment thereto of Dr. Edgar Douglas Adrian, a Fellow of our

Society and of Trinity College, Cambridge, and hitherto Lecturer in Physiology in that University. Dr. Adrian has already a distinguished record as an investigator, especially in the physiology of the nervous system. In recent years, with the aid of apparatus using the modern means of electrical amplification, he has been engaged in recording and analysing the minute changes transmitted, from an excited peripheral sense-organ, along the conducting system of the nerves—changes which, on arrival at a nerve-centre in the brain of a conscious being, would result in one or another form of sensation. In this, or in other important fields of investigation, we may wish Dr. Adrian a long and fruitful use of that greater freedom for research which our Royal Society Professorships afford. Dr. Adrian will for the present continue his researches in the Physiology Laboratory, Cambridge.

In my address last year, I referred to recent advances in the production of very high voltages for technical purposes, and the application of these voltages to highly exhausted tubes in order to obtain a copious supply of high-speed electrons and atoms and high-frequency radiation. It is of interest to note how rapidly in recent years our ideas have widened as to the possibilities of production of very high-frequency radiation of the X-ray type, both by artificial and natural processes.

In my address this afternoon, I shall briefly consider the present state of our experimental knowledge on this subject, and the various directions of attack by which we may hope to get further information. On the quantum theory, the energy associated with a quantum of radiation of frequency $\nu$ is given by $h\nu$, where $h$ is the well-known constant of Planck. When swift electrons impinge on matter, radiation of an X-ray type is generated over a wide range of frequencies, and it has been verified experimentally that the maximum frequency of the radiation obtainable in this way is limited by the relation $E = h\nu$, where E is the energy of motion of the electron, a result in accordance with energy considerations.

For purposes of discussion, it is very convenient to express the energy of a quantum not in ergs but in terms of a potential difference in volts, through which an electron must fall to acquire an equal energy. Expressed in this way, the energy of a quantum of green light corresponds to 2 electron-volts, or 2 volts for brevity. Before the advent of X-rays, the highest frequencies examined were confined to the ultra-violet part of the light spectrum, corresponding to less than 10 volts. Following the discovery of X-rays and the application of methods for determining their frequency, we have been enabled to study radiations over a wide range of individual energy, varying from a few hundred volts to 300,000 volts or more. By the use of special gratings and other methods, the gap in frequency between ordinary ultra-violet light and soft X-rays has been bridged in the last few years. There appears to be no limit to the maximum frequency that can be obtained by the bombardment of matter with electrons, except the practical difficulty of obtaining streams of the requisite high-velocity electrons. In some recent experiments in the Institute of Technology, Pasadena, about 1 million volts has been successfully applied for a short time to a suitably designed X-ray tube. It is stated that the X-rays obtained were of such intensity and penetrating power that they could easily be observed by the luminosity on a phosphorescent screen 100 feet away.

So far our experiments in this direction have been limited to about 1 million volts, and we have not yet been able to produce X-rays in the laboratory of penetrating power equal to that shown by the gamma-rays spontaneously emitted by radioactive bodies. The highest frequency observed in their transformations corresponds to between 3 and 4 million volts. Some recent experiments indicate that the gamma-rays which accompany the weak radioactivity of potassium are of still greater penetrating power than the rays from radium, but no definite estimate of the maximum frequency has so far been made.

There is, in addition, another general method of estimating the frequency of radiation that may arise in certain fundamental atomic processes of a simple type. According to modern views energy and mass are closely connected, and the relation between the energy E resident in a mass $m$ is given by the well-known equation of Einstein $E = mc^2$, where $c$ is the velocity of light. According to this view, if any system decreases in mass by internal rearrangement, the total energy lost in the process is given by the product of the change of mass multiplied by $c^2$. If this energy is emitted in the form of a radiation of one definite frequency $\nu$, then $h\nu = c^2dm$, where $dm$ is the accompanying change of mass of the system. On account of the very small change of mass even for a large emission of energy, it is difficult to give a direct experimental proof of this relation, but there seems to be little doubt of its general validity. Even for the radioactive bodies, which in their successive transformations spontaneously emit a very large amount of energy per atom, in the form of alpha-, beta- and gamma-rays, the effect to be expected is small and difficult to measure. The atom of uranium, of mass about 238, after successive transformations involving the loss of eight alpha-particles changes into an isotope of lead, of mass about 206.

It is to be anticipated, that, if the methods of positive ray analysis could be applied to these elements, the difference between the atomic masses of uranium and the resulting lead would include not only the mass of 8 helium nuclei in the free state, but also about 0·05 unit of atomic mass, corresponding to the total emission of energy of about 46 million electron-volts per disintegrating atom of uranium. This difference—about 1 in 4,000—should be just detectable by the methods employed by Aston in his study of isotopes. Similarly the change of mass in each transformation can be deduced if the energy released during the process is known experimentally.

We shall now consider the application of these ideas to certain nuclear processes. It is now generally accepted that the nuclei of all the elements are composed of protons (hydrogen nuclei) and electrons. While it is of course difficult to give a definite proof of this hypothesis, we know that it is strongly supported by the work of Aston on the atomic masses of the isotopes of the elements, and by the experiments on the liberation of protons from certain light elements when bombarded by swift alpha-particles. It is generally supposed that the helium nucleus is composed of a close combination of four protons and two electrons. The mass of the helium atom is 4·00216 (O = 16), while the mass of four hydrogen atoms in the free state is 4 × 1·0078. There is in consequence a loss of mass of 0·029 units in the formation of the helium atom. This indicates a loss of energy of 27 million electron-volts in the process of building a helium nucleus from free protons and electrons. If it be possible to imagine that in some way this energy is emitted catastrophically, in a single quantum of radiation, the energy of the quantum would correspond to 27 million volts. The energy emitted per atom is thus very large, and it has been suggested by Eddington and others that the formation of helium from hydrogen nuclei and electrons may be one of the sources of the energy radiated from the stars.

In a similar way the total energy emitted during the formation of any atom of known mass from free protons and electrons may be estimated. Since the proton in a free state has a mass 1·0073, and a mass about 1·000 in the average nuclear combination, the energy released per proton is about 7 million volts. For example the atomic weight of the most abundant isotope of mercury (atomic number 80) is 200·016, and this presumably contains 200 protons, of mass nearly unity, and 120 electrons. Disregarding the small mass due to the electrons, we may conclude that the total energy emitted during the formation of a mercury atom from free protons and electrons is about 1400 million electron-volts.

When we consider the extreme complication of such a heavy nucleus and the number of its component parts, it is difficult to believe that this emission of energy can take place in one single catastrophic act. It is so much more likely that the energy is emitted in a step by step process during the organisation of the nucleus. Except for light atoms, where the nuclear structure is simple, it is to be expected that the radiation of energy from all complex nuclei would occur in successive stages.

On the other hand, there is one possibility to consider, which was first put forward by Jeans to account for the long lives of the hot stars. He supposes that even the protons and electrons are not indestructible, but may under unknown conditions be transformed into radiation. The total internal energy of the electron is about 500,000 volts, but of the proton 1,840 times greater, or about 940 million volts. If we suppose the proton and electron to disappear together in the form of radiation, there must be an enormous liberation of energy. If this energy be emitted in a single quantum, we should expect to obtain a gamma-radiation corresponding to about 940 million volts. Such an hypothesis is admittedly of a very speculative nature and may be very difficult of direct proof or disproof.

Apart from the radioactive bodies, we have no definite experimental evidence of the emission of penetrating radiations, either in the formation of atoms or destruction of protons, and it may be that the processes considered do not take place under the conditions of our experiments on the earth. On the other hand, the long life of the hot stars indicated by general astronomical evidence does seem to demand some such process or processes, in which the liberation of energy is enormous compared with the mass involved.

It is thus of very great interest to examine whether any direct experimental evidence can be obtained of the existence of such extraordinarily energetic gamma-rays. This interest is heightened by the experiments in recent years which have shown the existence of an extremely penetrating type of radiation, sometimes called the "cosmic" rays, in our atmosphere—a radiation much more penetrating than the gamma-rays from the radioactive bodies. This radiation has been detected and measured by the small ionisation produced in a closed electroscope. The initial observations were made by Hess and by Kolhôrster, and we owe much to the admirable experiments of Millikan and Cameron, who have carefully examined the absorption of this radiation by the water of mountain lakes, which are practically devoid of ordinary radioactive matter.

It is clear from these experiments that the radiation is complex in character, and that there are present radiations which are able to pass through 17 metres of water for a reduction of intensity to one-half value. It is natural to suppose that this radiation is of a gamma-ray type, but it should be borne in mind that the effects so far observed would be equally explicable if the radiations consisted not of high-frequency gamma-rays, but of high-energy electrons entering our atmosphere.

Assuming, however, that the radiation is of the gamma-ray type, it is necessary to consider the factors that determine the absorption of such a radiation by matter. During the past 20 years, the problem of the nature on the absorption of X-rays and gamma-rays by matter has been the subject of detailed investigations, and there is now a general consensus of opinion on the main features of the processes involved. In the case of the heavier elements, the absorption of ordinary X-rays is mainly due to the interaction between the radiation and the electrons in the atom, whereby the energy of the quantum of radiation is transferred to the electron. This is generally known as the "photoelectric" effect. In addition there is a relatively small loss of energy due to the scattering of the incident radiation by the electrons; but in general, except for very high-frequency X-rays and light elements, the absorption due to the photoelectric effect predominates. The case is quite different when we deal with penetrating gamma-rays, where the loss of energy due to the process of scattering becomes relatively much more important, and for radiation of energy of the order of 100 million volts almost completely governs the absorption.

The main features of this scattering, known as the Compton effect, are now well understood. There is an occasional interaction between the quantum of radiation and the electron in an atom, whereby the radiation is scattered and the electron set in motion. The scattered radiation is always of lower frequency then the incident radiation, the difference depending on the angle of scattering. In this type of encounter between radiation and an electron, both momentum and energy are conserved, and consequently the energy given to the electron depends on the nature of the encounter, and thus on the angle of scattering of the radiation. The essential correctness of this theory has been verified by several distinct methods.

When a pure radiation of definite frequency is passed through matter, there always remains some transmitted radiation which has not been transformed, but mixed with it are degraded radiations of much lower frequency and swift electrons set in motion by the process of scattering. The ionisation observed in a closed vessel is probably mainly due to the electrons liberated by scattering in the medium and the walls of the containing vessel.

Assuming that the laws of the Compton process of scattering are valid for high-frequency radiation, there still remains the difficulty of estimating the probability of such scattering encounters, for on this probability depends the actual magnitude of the absorption coefficient. Different methods of calculating this probability have been given by A. H. Compton, Dirac, and recently by Klein and Nishina. The theory of Compton is based mainly on classical analogies, and that of Dirac on the earlier quantum mechanics. Recently the problem has been attacked again by Klein and Nishina (' Nature,' Sept. 15, 1928), using the later relativistic form of wave-mechanics formulated by Dirac. The calculated absorption coefficients for high-frequency radiations differ materially from one another on these three theories, and in particular the theory of Klein and Nishina gives a greater absorption coefficient for a given high-frequency radiation. For radiations of individual energy more than 100 million volts, the coefficient is about five times greater than that given by the formula of Dirac.

Unfortunately the experimental evidence available from a study of the absorption of the most penetrating gamma-rays from radioactive bodies is not complete enough to give a definite test of the validity of these theories. However, Mr. Gray, of the Cavendish Laboratory, who has made a careful examination of existing data on the absorption of gamma-rays, informs me that the evidence as a whole is more in accord with the theory of Klein and Nishina than with the earlier theories of Compton and Dirac. It is evident, however, that in view of the importance of the question, a careful determination is required of the absorption and scattering of gamma-rays, of as definite frequency as possible, in order to distinguish between the various theories.

It is of interest to note that the absorption coefficient of the most penetrating type of radiation, deduced by Millikan and Cameron from their experiments, is in excellent accord with that to be expected on the Klein-Nishina theory for a quantum of energy 940 million volts—the energy demanded for the transformation of the internal energy of the proton into radiation. Although this agreement is suggestive, our theories of absorption are at present too uncertain to place much weight upon it. Even if subsequent experiment should prove the correctness of an absorption formula within a certain range of frequency corresponding to the gamma-rays there would still be the need of extrapolating the formula over a very wide range, say from quantum energies of 3 million volts to 1,000 million volts, to include the ultra-penetrating rays observed in our atmosphere.

In addition there are a number of new factors which may have to be taken into consideration when we are dealing with the passage of very high-frequency radiation through matter. In the ordinary theories, the scattering of the radiation is supposed to be confined to the extra-nuclear electrons, but if we are dealing with a quantum of energy corresponding to the order of 100 million volts, it is not unlikely that the nuclear electrons may be effective in scattering as well as the outer electrons. Such an effect is to be expected if the energy of the quantum is large compared with the energy required to release an electron from the nucleus. In addition there is always the possibility, and even the probability, that such energetic radiations or the swift electrons liberated by them may be able occasionally to disintegrate the nucleus of the atom in their path.

For all these reasons, it is evident that much more information is required before we can draw any but tentative conclusions as to the nature of the penetrating radiations in our atmosphere. So far, experiments have been mainly confined to measuring the ionisation produced in a sealed electroscope. Further experiments are required, which will give us definite indication of the energy of the swift electrons present in the atmosphere, for this will give us valuable information on the maximum frequency of the radiation present, quite independently of the exact accuracy of our theories of absorption.

Continued observations made in a Wilson expansion chamber should throw much light on the nature of the particles which produce the ionisation in a closed vessel, and with the addition of a magnetic field of sufficient intensity the curvature of the tracks of beta-rays should enable us to determine their individual energy. Experiments of an analogous kind have already been made with an expansion chamber by Skobelzyn, in order to determine the relative intensities of the main gamma-rays emitted by radium C. In the course of these experiments, he has observed on several occasions the trails of very energetic beta-particles, probably arising from the ultra-penetrating radiation in our atmosphere.

During the present year Prof. Hans Geiger has developed a modified form of beta-ray counter, which records each beta-particle entering a vessel of considerable volume in any direction. This new method is so delicate that it may prove very useful in counting and even recording the number of beta-particles produced by the penetrating radiation. While it is to be hoped that in the years to come we may have available for study in our laboratories swifter beta-rays and higher-frequency radiation than we have to-day, we can hardly hope in the near future to produce artificially radiations, atoms and electrons which have an individual energy of the order of 100 million to 1000 million volts, such as are present in our atmosphere.

It is thus of great interest and importance to use every promising method of attack to throw light on the nature and origin of these penetrating radiations and the effects arising in their transmission through matter. The magnitude of the effects to be observed is small and not easy to measure with accuracy; but with the ever-increasing delicacy of methods of attack we may hope to gain much further information. The study of these extraordinarily penetrating radiations is not only of great interest in itself, but also for its promise of throwing new light on fundamental processes in our universe connected with the building up and destruction of atoms. It may take many years of faithful experiment before the evidence is sufficient to test the correctness of the numerous interesting speculations that have been advanced to account for the origin and nature of these radiations.

We now pass to the presentation of the medals.

The Copley Medal is awarded to Sir Charles Parsons, O.M., F.R.S.

In the world of mechanical engineering the genius of Charles Parsons has opened up a new era. He has originated and developed a new type of thermal engine entirely flexible and adaptable, and capable of high efficiency, combined with concentration of power never even imagined before.

By continuous practical effort for the past 45 years, aided by remarkable mathematical insight acquired in his University days, he has perfected the parallel-flow compound steam turbine, and has applied it successfully to electric generation and to marine propulsion, both attaining to an unprecedented scale. In this progress there have been involved great ingenuity in practical design and careful research into the dynamics of the flow of steam between fixed and moving blades, and the scientific determination of the best proportions for the successive stages of expansion and the degrees of superheating. The result has been that while the utilisation of heat in the best triple-expansion reciprocating steam engine amounts to 17 per cent. of the whole, the Parson's large central station turbines now convert 25 per cent. into mechanical power, and in still larger turbines 28 per cent. is anticipated.

The first steam turbine of 4 kilowatts was used in 1885 for electric lighting. This was followed by the development of turbines of increasing power, reaching 5,000 kilowatts in 1910. At present turbines of 20,000 and 30,000 kilowatts are in operation.

The application to marine propulsion was signalised in 1897 by the appearance of the "Turbinia," a small experimental craft of 200 tons, developing the extraordinary speed of 33 knots. Large turbine-driven destroyers for the Navy rapidly followed. In 1904 the cruiser "Amethyst," of 3,000 tons, was propelled by Parsons turbines of 14,000 h.p., with success so conspicuous that all new warships of all classes were fitted with steam turbines, so that by 1912 the Royal Navy had 7 million horse-power of Parsons turbines in operation. In the merchant navy progress was equally rapid. The first turbine vessel was the Cunard liner "Carmania," and now all large high-speed liners, such as the "Aquitania," are turbine-driven.

During this remarkable development numerous problems arose, urgently demanding a solution, involving a precise study of jet velocities, leakage, turbulent flow and vacuum augmenters. The phenomena involving cavitation of screw propellers opened up new fields, of abstract as well as practical interest.

Naturally other eminent inventors have taken a share in this progress, but they would doubtless all concur that Sir Charles Parsons has been greater in the scientific development of thermal power produced by steam than any engineer since James Watt.

A recent side-product of Sir Charles Parsons' activities, here stimulated by heredity, has been the revival of the British scientific industry, once conspicuous, of optical glass and telescopic construction, while some of his hours of relaxation have been spent in the strenuous endeavour to crystallise carbon into diamonds by catastrophic processes.

The Rumford Medal is awarded to Prof. Friedrich Paschen.

Prof. Paschen is especially distinguished for his important contributions to spectroscopy. He early acquired remarkable skill in the investigation of infra-red radiation and made valuable determinations of the distribution of energy in the spectrum of a black body, giving the first experimental proof of the law that the frequency of maximum energy is proportional to the absolute temperature. He afterwards made numerous observations of the infra-red emission spectra of various elements, which were of fundamental importance for the development of our knowledge of series in spectra, and subsequently for the theory of spectra in relation to atomic structure.

Prof. Paschen has also contributed in a notable degree to the precise measurement and series classification of spectrum lines in general. His masterly analysis of the highly complicated spectrum of neon affords an admirable example of his insight and skill. His work on the spectrum of doubly-ionised aluminium also stands out conspicuously as giving the first proof of Bohr's deduction that the series in such a spectrum should be characterised by a constant nine times greater than the Rydberg constant which is applicable to the spectra of neutral atoms. Another striking contribution was made by his extremely delicate observations of the fine structure of the lines of ionised helium, which proved to be in close agreement with Sommerfeld's theory, and led to one of the most trustworthy estimates of the mass of an electron. Prof. Paschen has also long been one of the foremost workers on the Zeeman effect, and the results which he has obtained, including the discovery of the well-known Paschen-Back effect, have been invaluable for theoretical discussions.

In all his investigations Prof. Paschen has shown extraordinary skill in the design and manipulation of apparatus, and the whole of his work is characterised by an obvious striving for the greatest attainable precision.

A Royal Medal is awarded to Prof. Arthur Stanley Eddington, F.R.S.

The contributions to knowledge of Prof. Eddington within the past ten years have been mainly in connection with the internal constitution of stars and with the generalised theory of relativity.

By an examination of the conditions of equilibrium of a typical giant star he showed that these were more easily satisfied when account was taken of radiation pressure. His results were somewhat modified when the extent of the ionisation at the high temperature in the interior of a star was pointed out by Jeans and Newall. He formulated a complete theory of the internal structure of a star, assumed to be a non-rotating whirl of atoms and electrons, with radiation gradually forcing its way to the surface; further, he pointed out that the masses of stars, which are found by observation not to vary greatly, ranged about the point where radiation pressure balances gravitation. Later, Eddington obtained a theoretical relation between the mass and absolute luminosity of giant stars. Taking Capella as a starting point, he found agreement with his theoretical results not only among giant stars but also among dwarfs, which had hitherto been supposed to have a liquid or solid nucleus; and he explained this result as due to the closer packing that is possible when atoms are stripped of their outer electrons. The companion of Sirius is the extreme example of this condition.

Eddington has also worked out a mathematical theory of Cepheid variables on the assumption that they are oscillating radially. These extremely bright stars play a fundamental part in several astronomical questions, and it is of the greatest importance that their physical condition should be investigated.

In connection with the theory of relativity, he conducted in 1919 one of the two eclipse expeditions which verified the deflection of light rays from stars near the sun. He also developed the theory, to a certain extent on the philosophical side, but considerably on the analytical side, especially with regard to the electromagnetic and gravitational fields.

Prof. Eddington has attained international fame by the brilliance of his contributions to astronomical science.

A Royal Medal is awarded to Dr. Robert Broom, F.R.S.

During the course of thirty-three years' search in Australia and South Africa Dr. Broom has made a very large number of important discoveries in vertebrate palæontology, embryology and morphology that shed new light upon the problems of the origin of mammals, lizards, crocodiles and birds, the significance of which has been interpreted in his Croonian Lecture ('Phil. Trans.,' 1914) and 285 memoirs. His researches represent the most significant contribution made by any one investigator to the determination of the relationships of the main groups of vertebrate animals, and to the definition and solution of the problems involved in the evolution of the higher groups.

At the time when he first went to South Africa, 35 genera and 65 species of fossil reptiles had been identified in the Karoo beds; very little was known of their structure, and the classification was in a state of apparently hopeless confusion. He tripled the number of known genera and quadrupled the number of species. He worked out the details of the anatomy of most of the groups, and established an orderly classification which has now been universally accepted by the scientific world. He is now actively engaged in the investigation of some of the outstanding problems involved in the evolution of mammals and birds.

The Davy Medal is awarded to Prof. Frederick George Donnan, F.R.S.

Prof. Donnan is, like his master van't Hoff, a man of ideas. Early in his scientific career he wrote on the nature of soap emulsions and on the theory of capillarity and colloidal solutions. Being thus engaged with problems of surface activity, and being also intimately conversant with the electrolytic dissociation hypothesis, he put two and two together and made thereby not four, but a multitude—the mark of original scientific genius. His theory of membrane equilibrium and membrane potential is an achievement of the first rank, and has been the starting-point of numerous studies not only in the domain of pure chemistry, but more especially in biochemistry, where the conditions for displaying the phenomena he predicted are often encountered. Physiological chemists have seized on his idea and utilised it in many fields of investigation.

Donnan's researches on surface tension and adsorption at liquid-liquid interfaces have led to results of the greatest interest, and his verification by means of nonylic acid of the Gibbs' adsorption formula is a most brilliant experimental conception. A by-product of Donnan's activities during the War is a theory of the action of gas-scrubbers, based on the velocity of absorption of gases by liquids.

Not only has Donnan by his own researches done the highest service to his science—he has founded a school of physical chemistry, whence issues a steady flow of admirable researches, which he has suggested, and of young physical chemists, whom he has inspired.

The Darwin Medal is awarded to Dr. Leonard Cockayne, F.R.S.

The award of a Darwin medal to Dr. Cockayne is fitting because of the distinction of his work in fields in which Charles Darwin himself laboured. That distinction has been gained by the use of the Darwinian method: a true naturalist, Dr. Cockayne has waited patiently upon facts before drawing conclusions. For over thirty years he has made it his task to deepen and widen our knowledge of New Zealand botany in the broadest sense. He has not only worked himself with outstanding ability and untiring energy; he has imparted his enthusiasm to a school of younger colleagues, eager to advance his labours on the lines he has laid down. The excellence of Dr. Cockayne's work, from the ecological point of view, is recognised by botanists in every country and has made him one of the foremost living students of plant-association; the taxonomic studies rendered necessary by his ecological results have led to those remarkable discoveries of natural hybrids in New Zealand that have won for him a world-wide reputation, and have made on modern thought an impression akin to that produced by the results of Mr. Darwin's studies of plants under domestication. Dr. Cockayne's researches have had, on sylvicultural and agricultural procedure, a practical bearing which has been appreciated by, and has influenced the policy of, New Zealand statesmen.

The combination of philosophic outlook and lucid exposition that marks his contributions to natural knowledge, may also explain the invitation, accepted by Dr. Cockayne, to contribute a monograph on the flora of New Zealand to

'*Die Vegetation der Erde*,' edited by Dr. Engler—a compliment no other British botanist has been paid. It does at least account for the remarkable local effect of Dr. Cockayne's book 'New Zealand Plants and their Story.' An eminent Continental ecologist, well acquainted with the philosophic importance of Dr. Cockayne's labours, has said "it is wonderful how Cockayne has succeeded in interesting the population of a new country in botany."

The Sylvester Medal is awarded to Prof. William Henry Young, F.R.S.

Dr. W. H. Young has taken a very prominent part in the development of the modern theory of functions of real variables, and in its application to the theory of Fourier's and other series. During the present century he has published an immense number of memoirs and notes dealing with this branch of mathematics and containing important advances in the subject; many of these are strikingly original, and even the smaller of them throw light on some particular points. His earlier work dealt chiefly with the theory of sets of points, and contains important developments on the lines laid down by G. Cantor and Harnack. He soon proceeded to apply this theory in the integral calculus, and he obtained a general definition of the integral which is essentially equivalent, although somewhat less simple in form, to that given, about the same time, by H. Lebesgue, which latter has become a corner stone of modern analysis. Much of Dr. Young's work has also proved to be a starting point for further investigations by other mathematicians. Instances of this feature in his work are his generalisations of the theorems of Parseval and Riesz-Fischer in the theory of Fourier's series; his investigations on the properties of Fourier's constants and of the series conjugate to Fourier's series. By means of his conception of restricted Fourier's series he was enabled to devise a method by which conditions of convergence, summability, &c., known to hold good for Fourier's series, could be carried over to series of Legendre's and Bessel's functions. Many other investigations in the domain of integration and Fourier's series, too numerous to be mentioned in detail, have contributed notably to our present knowledge in this department of analysis.

The Hughes Medal is awarded to M. Le Duc de Broglie.

Maurice François César, Duc de Broglie, member of the Academy of Sciences, is distinguished especially for his pioneer researches on X-ray spectra and secondary beta-rays. He was one of the first to obtain the complete emission spectrum of X-rays and to study X-ray absorption spectra, while his work on the magnetic spectrum of the beta-rays, arising from the passage of X-rays through matter, has proved of great importance. He founded in Paris a private laboratory directed by him, which is devoted to researches on X-rays and allied subjects. An experimeter of unusual skill, he and his co-workers have made important contributions to knowledge in many fields.

# *The Production of New Radiations by Light Scattering.—Part* I.

By Prof. C. V. RAMAN, F.R.S., and K. S. KRISHNAN.

(Received August 7, 1928.)

(PLATES 1, 2.)

## 1. *Introduction.*

In two preliminary papers* we have recorded the discovery that when monochromatic light is scattered in a transparent medium (be it gas, vapour, liquid, amorphous solid or crystal), the diffused radiation ceases to be monochromatic, and several new lines or sometimes bands (associated in many cases with a continuous spectrum) appear in the spectrograms of the diffused radiation. Further, the new radiations are, in general, strongly polarised. That the phenomenon is entirely distinct from what is usually known as fluorescence is clear from the fact that the effect is observed when both the exciting radiation and the new radiations generated by it are far removed from the characteristic ultra-violet and infra-red frequencies of the medium. As an illustration we may mention the case of transparent crystalline quartz in which the effect is very well shown with the 4358 A.U. line of mercury as the exciting line, the new lines also appearing in the indigo-blue region of the spectrum. Our preliminary studies have proved conclusively that the effect arises in the following way: The incident quantum of radiation is either scattered as a whole, in which case we have the classical scattering, or else is absorbed in part by the molecules of the medium, the remaining part appearing as a scattered quantum. The part absorbed shifts the molecule to a level of energy different from the initial state. The possibility of a process of this kind, in respect of the electronic state of an atom, was first contemplated by Smekal,* and figures prominently in the theory of dispersion due to Kramers and Heisenberg,† and in the papers of Schrödinger.‡ Our experiments furnish definite proof of the possibility of such processes, and show that they may occur also in such complicated systems as the molecules of a vapour or a liquid or even in a complete crystal. In the series of papers of which this is the first our further studies of the new radiations will be discussed.

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* Raman, 'Ind. J. Phys.,' vol. 2, p. 387 (1928); Raman and Krishnan, 'Ind. J. Phys.,' vol. 2, p. 399 (1928).

### 2. *Experimental Methods.*

The experimental arrangements were exactly the same as those described in the previous papers. The liquids to be examined were rendered dust-free in the usual manner by repeated slow distillation *in vacuo*, and the final distillate was contained in a bulb of about 500 to 600 c.c. capacity. A 3000-c.p. mercury arc served as the source of monochromatic illumination and was concentrated with an 8-inch condenser, at the centre of the liquid bulb, which was kept immersed in a suitably blackened glass tank containing water. By interposing a strong solution of quinine sulphate and a plate of blue glass between the condenser and the liquid, practically all the lines of the incident mercury spectrum excepting the 4358·3 line and its close companions were cut out. In the case of carbon tetrachloride, where the modified lines were sufficiently close to the exciting line, no filters were used.

The spectrum of the scattered light was taken with a Hilger quartz spectrograph ($E_2$), using very rapid photographic plates (Ilford Iso-zenith, H. & D. 700). In the case of the single line pictures of benzene and toluene an exposure of about 40 hours was necessary, while for carbon tetrachloride, for which the complete mercury arc was incident, an exposure of only 25 hours was given.

### 3. *Experimental Results.*

In Plates 1 and 2 are reproduced the spectrograms of the scattering by benzene, toluene and carbon tetrachloride. The plates were measured with a Hilger travelling micrometer and the wave-lengths of the modified lines were calculated, using the mercury lines (feebly transmitted by the filters) as standards for reference. A simplified Hartmann formula was used for interpolation.

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* 'Naturw.,' vol. 11, p. 873 (1923).

† 'Z. Physik,' vol. 31, p. 681 (1925).

‡ 'Abhandlungen zur Wellenmechanik,' Leipzig, p. 112 (1927).

Table I.—Spectrum of Benzene Scattering.

| Unmodified Lines. | | | Modified Lines. | | | Origin of the Modified Lines. | |
|---|---|---|---|---|---|---|---|
| Wave-length I.A. | Wave-number (*in vacuo* per cm.) | Intensity. | Wave-length I.A. | Wave-number (*in vacuo* per cm.) | Intensity. | Wave-length of the exciting line. | Difference of wave-numbers. |
| | | | 4178·0 | 23928 | 0 | 4358·3 | — 990 |
| | | | 4246·7 | 23541 | 0 | 4358·3 | — 603 |
| 4339·2 | 23039 | 15 | | | | | |
| 4347·5 | 22995 | 30 | | | | | |
| 4358·3 | 22938 | 200 | | | | | |
| | | | 4476·4 | 22333 | 1 | 4358·3 | 605 |
| | | | 4525·8 | 22089 | 0 | 4358·3 | 849 |
| | | | 4534·5 | 22047 | 0 | 4339·2 | 992 |
| | | | 4543·4 | 22004 | 0 | 4347·5 | 991 |
| | | | 4555·1 | 21947 | 10 | 4358·3 | 991 |
| | | | 4593·9 | 21762 | 2 | 4358·3 | 1176 |
| | | | 4683·5 | 21346 | 1 | 4358·3 | 1592 |
| | | | 5020·6 | 19877 | 1<br>Broad | 4358·3 | 3061 |

Table II.—Spectrum of Toluene Scattering.

| Unmodified Lines. | | | Modified Lines. | | | Origin of the Modified Lines. | |
|---|---|---|---|---|---|---|---|
| Wave-length I.A. | Wave-number (*in vacuo* per cm.) | Intensity. | Wave-length I.A. | Wave-number (*in vacuo* per cm.) | Intensity. | Wave-length of the exciting line. | Difference of wave-numbers. |
| | | | 4176·1 | 23939 | 0 | 4358·3 | — 1001 |
| | | | 4213·7 | 23725 | 0 | 4358·3 | — 787 |
| | | | 4262·3 | 23455 | 0 | 4358·3 | — 517 |
| | | | 4315·6 | 23165 | 1 | 4358·3 | — 227 |
| 4339·2 | 23039 | 15 | | | | | |
| 4347·5 | 22995 | 30 | | | | | |
| 4358·3 | 22938 | 200 | | | | | |
| | | | 4399·5 | 22723 | 2 | 4358·3 | 215 |
| | | | 4424·9 | 22593 | 1 | 4358·3 | 345 |
| | | | 4448·4 | 22474 | 0 | 4347·5 | 521 |
| | | | 4459·3 | 22419 | 2 | 4358·3 | 519 |
| | | | 4479·8 | 22316 | 1 | 4358·3 | 622 |
| | | | 4501·7 | 22208 | 0 | 4347·5<br>4358·3 | 787<br>730 |
| | | | 4512·8 | 22153 | 4 | 4358·3 | 785 |
| | | | 4547·1 | 21986 | 0 | 4347·5 | 1009 |
| | | | 4558·0 | 21933 | 7 | 4358·3 | 1005 |
| | | | 4563·0 | 21909 | 1 | 4358·3 | 1020 |
| | | | 4591·0 | 21776 | 1<br>Broad | 4358·3 | 1162 |
| | | | 4600·8 | 21729 | 2 | 4358·3 | 1209 |
| | | | 4638·0 | 21555 | 1 | 4358·3 | 1383 |
| | | | 4648·3 | 21507 | 0 | 4358·3 | 1431 |
| | | | 4664·0 | 21435 | 0 | 4358·3 | 1503 |
| | | | 4685·5 | 21336 | 2 | 4358·3 | 1602 |
| | | | 4994·3 | 20017 | 0 | 4358·3 | 2921 |
| | | | 5027·3 | 19886 | 1 | 4358·3 | 3052 |

Table III.—Spectrum of Carbon Tetrachloride Scattering.

| Unmodified Lines. | | | Modified Lines. | | | Origin of the Modified Lines. | |
|---|---|---|---|---|---|---|---|
| Wave-length I.A. | Wave-number (*in vacuo* per cm.) | Intensity. | Wave-length I.A. | Wave-number (*in vacuo* per cm.) | Intensity. | Wave-length of the exciting line. | Difference of wave-numbers. |
| | | | 4273·5 | 23393 | 1 | 4358·3 | − 455 |
| | | | 4299·6 | 23251 | 2 | 4358·3 | − 313 |
| | | | 4317·2 | 23157 | 2 | 4358·3 | − 219 |
| 4339·2 | 23039 | 15 | | | | | |
| 4347·5 | 22995 | 30 | | | | | |
| 4358·3 | 22938 | 200 | | | | | |
| | | | 4400·3 | 22719 | 7 | 4358·3 | 219 |
| | | | 4418·5 | 22626 | 8 | 4358·3 | 312 |
| | | | 4447·3 | 22479 | 10 | 4358·3 | 459 |
| | | | 4509·3 | 22170 | 2 | 4358·3 | 768 |
| | | | 4514·0 | 22147 | 2 | 4358·3 | 791 |

## 4. *Infra-Red Spectra of the Molecules.*

As has been shown in our previous papers, the shift in frequency of the modified lines must correspond to a characteristic frequency of the molecule. In the following table are exhibited the shifts in wave-number of the different modified lines and the corresponding infra-red wave-lengths characteristic of the molecule. The infra-red absorption spectra of these liquids have been studied by Coblentz,* Bell† and others, and their values are also reproduced in the table for comparison.

Considering the uncertainties in the direct measurement of infra-red spectra, the agreement between the values of the characteristic wave-lengths calculated from light-scattering and those measured directly should be considered satisfactory; thus confirming the conclusions drawn in our previous papers regarding the origin of the modified lines.

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* Quoted by J. W. Ellis, 'Phys. Rev.,' vol. 27, p. 305 (1926).

† 'J. Am. Chem. Soc.,' vol. 47, p. 2814 (1925).

Table IV.—Infra-Red Spectra of the Molecules.

| Benzene. | | | Toluene. | | | Carbon Tetrachloride. | | |
|---|---|---|---|---|---|---|---|---|
| Shift in wave-number. | Infra-red wave-length. | | Shift in wave-number. | Infra-red wave-length. | | Shift in wave-number. | Infra-red wave-length. | |
| | Calculated. | Observed (Bell). | | Calculated. | Observed (Coblentz) | | Calculated. | Observed (Coblentz) |
| Cm.$^{-1}$ | μ | μ | Cm.$^{-1}$ | μ | μ | Cm.$^{-1}$ | μ | μ |
| 3061 | 3·27 | 3·3 | | | | | | |
| | | | 3052 | 3·28 | | | | |
| | | | 2921 | 3·42 | 3·4 | | | |
| | | | 1602 | 6·24 | 6·2 | | | |
| 1592 | 6·28 | 6·2 | | | | | | |
| | | | 1503 | 6·65 | | | | |
| | | | 1431 | 6·99 | 6·9 | | | |
| | | | 1383 | 7·23 | | | | |
| | | | 1209 | 8·27 | | | | |
| 1176 | 8·57 | 8·5 | | | | | | |
| | | | 1162 | 8·60 | 8·6 | | | |
| | | | 1029 | 9·71 | | | | |
| | | | 1005 | 9·94 | 9·9 | | | |
| 991 | 10·09 | 9·7<br>to<br>10·2 | | | | | | |
| 849 | 11·78 | 11·8 | | | | 791 | 12·64 | 13 |
| | | | 786 | 12·72 | 12·1 | | | |
| | | | | | | 768 | 13·02 | |
| | | | 730 | 13·69 | 13·9 | | | |
| | | | 622 | 16·07 | | | | |
| 605 | 16·52 | | | | | | | |
| | | | 520 | 19·23 | | | | |
| | | | | | | 457 | 21·9 | |
| | | | 345 | 29·0 | | | | |
| | | | | | | 312 | 32·0 | |
| | | | | | | 219 | 45·6 | |
| | | | 215 | 46·5 | | | | |

## 5. *Light Scattering and Infra-Red Spectroscopy.*

Attention was drawn in our previous papers to the usefulness of light scattering as a convenient and accurate method in infra-red spectroscopy. In a single spectrogram taken in the visible region we get all the infra-red frequencies of the molecule simultaneously photographed, and they could be measured much more accurately than with an infra-red spectrometer. For example, in the case of sharp, bright lines, as some of those appearing in the spectrograms are, we can, with an instrument of larger dispersion and using suitable comparison standards, measure them correct to a hundredth of an Ångström unit, which corresponds in the near infra-red, say, 3 μ, to an accuracy of about 1 part in 60,000, and in the extreme infra-red, say, 20 μ, to 1 part in 10,000. In fact, the accuracy is limited only by the width of the modified line.

The appearance in the scattered spectra of toluene and carbon tetrachloride of modified lines corresponding to several hitherto unknown frequencies of the molecules, in the extreme infra-red region as far as 46 $\mu$,* emphasises the ready applicability of the method especially to regions not accessible to the ordinary infra-red spectrometer.

### 6. *Enhancement of Frequency in Light Scattering.*

While most of the modified lines are of smaller frequency than the exciting line there appear in all the three spectrograms (figs. 2, 3 and 5) some relatively feeble lines whose frequencies *exceed* the frequency of the exciting line by an infra-red frequency of the molecule. These lines are particularly conspicuous in the case of carbon tetrachloride, where corresponding to each of the three prominent lines on the longer wave-length side of the exciting line we have a weaker line on the shorter wave-length side. The appearance of these lines of enhanced frequency proves in the first place the existence in the liquid at ordinary temperatures of some molecules at a level of energy higher than the normal by that corresponding to an infra-red frequency of the molecule, and secondly, that the incident light induces a return of these molecules to the normal state. That is to say, while most of the molecules taking part in modified scattering are in the normal state and absorb a part of the incident light quantum, thus giving rise to a scattered radiation of smaller frequency, there is also a small number in the liquid, already in the higher level of energy, which under the influence of the incident radiation can be induced to part with their energy by a return to the normal state, thus giving rise to a scattered radiation of correspondingly higher frequency. In the existence of these lines of enhanced frequency we have for the first time a direct experimental proof of *induced emission* of radiation by molecules.

It may be of interest to recall in this place that the idea of an induced emission of radiation or what has sometimes been described as a "negative absorption of radiation," was first put forward by Einstein in his celebrated paper† on the derivation of Planck's radiation formula, and forms an essential feature of his theory. The idea also figures prominently in the theory of dispersion developed by Kramers and Heisenberg (*loc. cit.*).

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* In fact in the case of toluene there is a line corresponding to even longer wave-lengths which could not, however, be measured in the particular negative.

† 'Phys. Z.,' vol. 18, p. 121 (1917).

The relative intensities of the positive and negative lines corresponding to a given molecular frequency $\nu$ can be easily calculated. The proportion of molecules in the higher level of energy is obviously given by the relation

$$f = e^{-\frac{h\nu}{kT}},$$

where $h$ is the Planck constant, $k$ is the Boltzmann constant per molecule, and T is the absolute temperature. If we assume, as we might reasonably, that the transitions of the molecule to and from the higher level are equally probable, then the above ratio, viz., $e^{-\frac{h\nu}{kT}}$ also represents the ratio of the intensities of the corresponding negative and positive lines.

Taking for example the case of carbon tetrachloride, corresponding to the shifts in wave number 219, 312 and 457 ($\text{cm.}^{-1}$) the calculated values for the ratio of intensities of the negative and positive lines are 1 : 2·8, 1 : 4·4 and 1 : 8·8 respectively, at the temperature of the experiment, viz., 30° C. Accurate measurements of the actual intensities of the lines have not been made. A rough estimate, however, of the intensities from the negative, using for comparison a series of graded exposures taken on the same negative and in the same region of the spectrum, gave the values 1 : 3, 1 : 5, and 1 : 10 respectively, in good agreement with the calculated values.

Conversely, we can take the observed intensity relationships between the different positive and the corresponding negative lines as an experimental verification of the assumption made in the earlier paragraph, that the forward and backward transitions of the molecule are equally probable. The probabilities of transitions of the molecule from the normal state to *different* energy levels are, of course, different, and the differences in the intensities of the different modified lines of degraded frequency are obviously due to this cause.

The rapid fall in the value of the ratio as $\nu$ increases offers a ready explanation why we do not get negative lines corresponding to large shifts of frequency. Also as the temperature is increased, since the proportion of molecules in a higher energy level also increases, we should expect the negative lines to brighten up relatively to the corresponding positive lines. Experiments are in progress to test this point.

### 7. *Continuous Spectrum accompanying the Scattered Lines.*

The molecular frequencies in the near and extreme infra-red, determining the shifts of the various modified lines discussed in the previous sections, are presumably vibrational frequencies. The question naturally arises whether we should not expect also shifts corresponding to the pure rotational frequencies of the molecules. For example, in the case of benzene, taking the rotational frequency of the molecule to be of the order of 100 $\mu$ the corresponding shifts for the 4358 line will be slightly less than 20 Å.U., and should be capable of being detected. A visual examination with a direct vision spectroscope, of benzene, toluene and some other liquids, showed a nebulosity or continuous spectrum accompanying the prominent lines in the scattered spectrum. The actual spectrograms reproduced here and in our earlier papers also show a general broadening of the lines. However, in view of the presence of a general photographic halation accompanying the bright lines—the plates used were not backed—we thought it desirable to take fresh pictures with a larger dispersion instrument, and they are reproduced here. Fig. 7 (Plate 2) shows the nebulosity accompanying the 4358 line scattered by liquid benzene, fig. 6 being the direct mercury spectrum diffused by a plate of ground glass, taken with the same instrument.* Fig. 8 shows the scattering by carbon tetrachloride where, however, the nebulosity is not so conspicuous as in benzene.

From the fact that in the case of benzene the extension of the nebulosity from the exciting line is of the same order of magnitude as the rotational frequency of the molecule, one is tempted, by analogy with the explanation of the origin of the modified lines, to attribute the nebulosity to a combination of the rotational frequencies of the molecule with the frequency of the incident radiation. Owing to the continual impedance to rotation which must be present in a dense medium, it is not difficult to understand why we get a continuous spectrum instead of discrete lines. In connection with this explanation it may be pointed out that the nebulosity extends unsymmetrically on the two sides of the exciting line, being more conspicuous on the longer wave-length side.

Whether the comparatively feeble continuous spectrum in carbon tetrachloride scattering is due to a smaller rotational frequency of the molecule or is in any way connected with its symmetrical nature, is more than we can venture to answer at present. Further observations, especially in the vapour state, or in the liquid at different temperatures, are obviously necessary before we can fully understand the origin of this nebulosity.

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* In this connection see an interesting paper by Cabannes and Daure, 'Comptes Rendus,' June 4, 1928.

### 8. *Polarisation of Scattered Radiations.*

In view of the imperfection in polarisation of the classical light-scattering at 90°, it becomes of importance to ascertain the nature of the polarisation of the modified radiations. For this purpose two spectrograms were taken with equal exposures and under identical conditions, side by side on the same plate, using a nicol in front of the slit of the spectrograph. During the first exposure the shorter axis of the nicol was perpendicular to the track in the liquid, and during the second, parallel to the track.

Fig. 9 gives the direct spectrum of the mercury arc, incident in the liquid, fig. 10 the scattered spectra of benzene, fig. 11 of carbon tetrachloride, and fig. 12 of amyl alcohol.

The following are some of the interesting results which emerge from a study of these spectrograms :—

(1) All the unmodified lines (*i.e.*, classical scattering) are polarised to practically the same extent.

(2) For a given shift of frequency, the modified lines excited by the different incident lines are polarised to the same degree, but differ in polarisation from the unmodified lines.

(3) The modified lines corresponding to different frequency shifts are polarised to different extents, the intensity of the weaker component varying from almost nothing to about 40 or 50 per cent. of that of the stronger line. For example, in the case of carbon tetrachloride, the most prominent modified line (which corresponds to a shift of 457 $\mathrm{cm.}^{-1}$) is more or less completely polarised, while the other two prominent lines show a large imperfection in polarisation.

(4) The negative lines (*i.e.*, of enhanced frequency) are polarised to the same extent as the corresponding positive lines.

(5) The strong modified lines are usually more polarised than the feeble ones.

(6) The general continuous spectrum appearing in the scattering by amyl alcohol is also strikingly polarised.

A tentative explanation of these results regarding the polarisation of the modified lines may be suggested by analogy with the ideas put forward by the late Lord Rayleigh and by Born to explain the observed imperfection of polarisation of the classical scattering. In the classical theory the molecules of the medium behave under the influence of the incident light-vector, like oscillating doublets, which, as a consequence radiate out energy. If the moment induced in the molecule is in the same direction as the inducing force, the transverse scattering would obviously be completely polarised. The imperfection in polarisation experimentally observed therefore suggests that there are three principal directions in the molecule mutually perpendicular to one another, only along which moments can be induced, and that to varying extents. If the incident force lies along any one of these directions the induced moment is along the same direction. In every other case we have to resolve the incident force along the principal axes of the molecule and then determine the corresponding moments induced in these directions. Incidentally, we may point out that on this basis, assuming the molecules to be independent scattering centres, as is very nearly the case in a gas, the ratio of the intensities of the two principal polarised components of the scattered light can never exceed 50 per cent., the latter limit being reached when the molecule is polarisable only along one axis.

Carrying now the analogy to the case of modified scattering let us tentatively assume that for a given energy transition of the molecule, there are three principal directions in the molecule, the Einstein coefficients of probability of transition under the influence of an external force incident respectively along these three directions being different. As regards the actual mechanism which leads to such an anisotropy we shall for the present leave it an open question. The imperfection in polarisation of the modified lines follows then as a necessary consequence. If, further, we take these principal axes, as well as the corresponding principal Einstein coefficients, to be different for different energy transitions of the molecule, the differences in the intensity and the degree of polarisation of the different modified lines are also readily explained. That for a given frequency shift the polarisation is independent of the inducing line is also obvious. The identity in the degree of polarisation of the positive and negative lines corresponding to a given frequency shift will then merely be a consequence of the equal probability of transitions in the positive and negative directions; that is to say, for the same reasons for which, as we pointed out in sec. 6, the intensities of the negative and positive lines are in the ratio of the number of molecules in a correspondingly higher level of energy, to the number in the normal state.

It is significant in connection with the above explanation that there is no modified line in the spectrograms for which the ratio of the intensities of the principal polarised components is greater than 50 per cent. Physically interpreted, this limiting value of the polarisation signifies that the vibration to which the frequency under consideration corresponds, can take place only along a definite axis in the molecule, which is *a priori* not improbable.

It remains now to discuss the relation between the polarisation of the unmodified radiations and that of the different modified ones. The modified radiations are presumably incoherent, *i.e.*, the radiations at any given instant from neighbouring molecules have no definite phase relationship, so that the polarisation of the modified radiation would be characteristic of the molecule and independent of its state of aggregation. On the other hand, the unmodified radiations from neighbouring molecules are definitely correlated in phase, and their polarisation will be characteristic of the molecule only in the vapour state. Actual calculation shows the polarisation in the liquid state to be considerably smaller. Thus for a fair comparison we should take the polarisation of the modified lines as given by the spectrograms with that of ordinary classical scattering not in the liquid but in the vapour. The vapour values for the ratio of components of classical scattering are benzene 4·5 per cent., amyl alcohol, 1·2 per cent., and carbon tetrachloride 0·5 per cent.

On making the actual comparison we find that most of the modified lines are much less polarised than the unmodified ones. If we can take the degree of anisotropy of the transitions corresponding to the infra-red frequencies as evidenced by the imperfection of polarisation of the corresponding modified lines, as being typical of the anisotropy of all other kinds of energy transitions of the molecule which determine its refractivity, especially the electronic transitions of ultra-violet frequencies, then the smaller polarisation of the modified lines is easily understandable; because the anisotropy of the molecule as a whole, which determines the polarisation of classical scattering, is merely a resultant of the anisotropies of all the individual transitions (suitably weighted) of the molecule, and must, therefore, necessarily correspond to a greater spherical symmetry.

### 9. *Dependence on Wave-Length.*

It is well known that the classical scattering falls off rapidly with increasing wave-length, following Rayleigh's $\lambda^{-4}$ law, and it will, therefore, be of interest to find how the intensity of the modified radiations depend on the wave-length of the exciting line. No quantitative measurements have yet been made which would enable us to decide this question. But we may draw attention here to the spectrogram of carbon tetrachloride scattering, which throws some light on the point. Comparing the intensities of the green $\lambda$ 5460·7 line and the ultra-violet $\lambda$ 3906·5 line of the mercury arc, as they appear in the spectrum of the scattered light the former line is much brighter, whereas comparing the modified lines excited by them, those excited by the green line are distinctly feebler than the ones excited by the ultra-violet line. It would thus appear that the intensity of the modified line changes with wave-length even more rapidly than is indicated by Rayleigh's inverse fourth-power law.

This is further confirmed by visual observations on the spectrum of scattered light with a direct vision spectroscope. Though as seen through the spectroscope the scattered green mercury line is far more intense than the indigo or violet lines, the modified lines excited by the green line could not be detected, whereas those due to the violet and indigo lines are very conspicuous.

### 10. *Summary.*

In two preliminary papers the authors have shown that when any transparent medium, be it gas, vapour, liquid, amorphous solid or crystal, is irradiated by monochromatic light the radiations scattered by the molecules contain several spectral lines of modified frequencies, the difference between the incident and scattered frequencies corresponding to a characteristic infra-red frequency of the molecule. The present paper describes further studies on these radiations.

(*a*) Using the $\lambda$ 4358 group of lines of the mercury arc as the exciting radiations, the scattered spectra of benzene, toluene and carbon tetrachloride have been photographed and measured.

(*b*) The characteristic infra-red frequencies of the molecules are calculated from the frequencies of the modified lines and are compared with the values obtained from direct measurements of infra-red absorption. The calculation gives several molecular frequencies hitherto unknown.

(*c*) The usefulness of light-scattering as a powerful, convenient and accurate method of exploring molecular spectra, is pointed out.

(*d*) While most of the modified lines are of smaller frequency than the exciting line, there are some relatively feeble lines whose frequencies exceed the frequency of the exciting line by an infra-red frequency of the molecule. In the appearance of these lines we have for the first time a direct experimental proof of *induced emission* (or negative absorption) of radiation by molecules.

(*e*) The scattered lines are sometimes accompanied by a nebulosity or continuous spectrum, extending unsymmetrically on the two sides. Its origin is discussed.

(*f*) The modified radiations scattered at 90° exhibit striking polarisation, the degree of polarisation being different for lines corresponding to different frequency shifts. A tentative explanation is suggested.

(*g*) Some preliminary remarks are made regarding the dependence of the intensities of the modified lines on the wave-length of the exciting line.

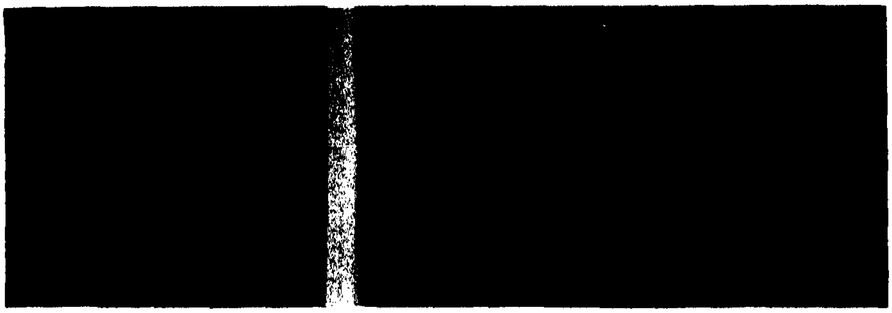

Fig. 1.—
Incident
Spectrum.

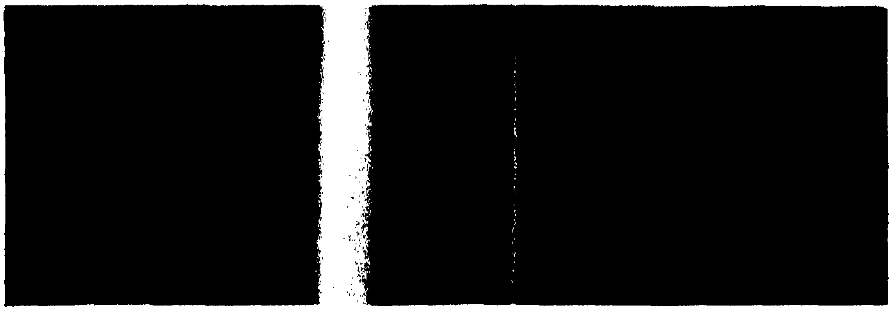

Fig. 2.—
Benzene
Scattering.

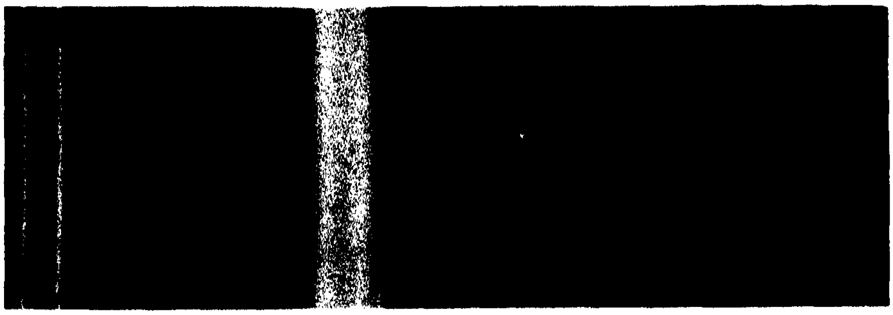

Fig. 3.—
Toluene
Scattering.

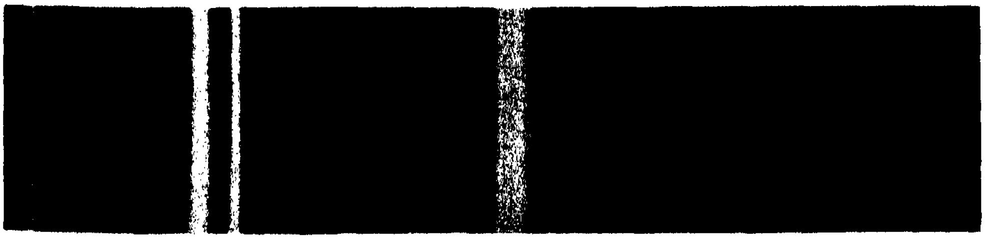

Fig. 4.—
Incident
Spectrum.

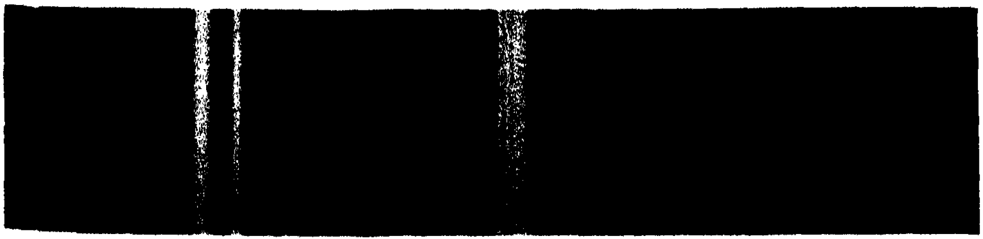

Fig. 5.
Carbon
Tetrachlori
Scattering.

**Fig. 6.**—Diffused by Ground Glass.

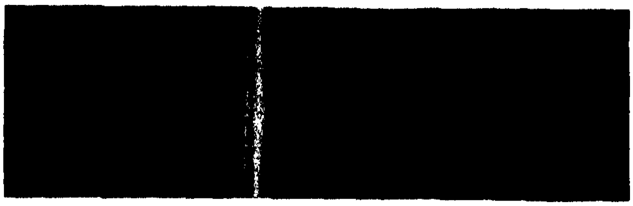

**Fig. 7.**—Scattered by Benzene.

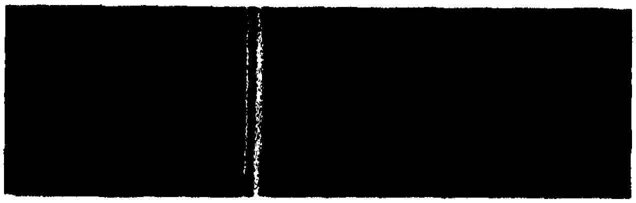

**Fig. 8.** Scattered by Carbon Tetrachloride.

Continuous Spectrum accompanying the Scattered Lines.

**Fig. 9.** Incident Spectrur

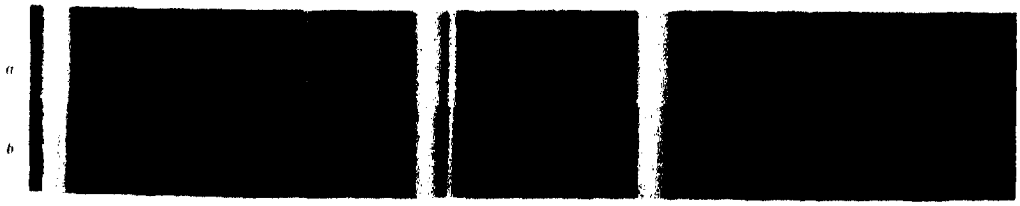

**Fig. 10.**—Benzene

**Fig. 11.**—Carbon Tetrach

**Fig. 12.** Amyl Alcohol.

## DESCRIPTION OF PLATES.

### PLATE 1.

FIG. 1 gives the spectrum of the mercury arc from which practically all the lines excepting the λ 4358 group have been cut out by interposing a solution of quinine sulphate and a blue glass plate.

FIG. 2 is the spectrogram of the radiations shown in fig. 1 when scattered by liquid benzene.

FIG. 3 is a similar spectrogram of the radiations scattered by toluene.

FIG. 4 is the direct spectrum of the mercury arc which was incident on carbon tetrachloride.

FIG. 5 being the corresponding scattered spectrum. Note the appearance of relatively feeble lines of enhanced frequency.

### PLATE 2.

FIG. 6.—Spectrum of the λ 4358 group of lines diffused by a plate of ground glass.

FIG. 7.—Spectrum of the same as scattered by benzene. Note the nebulosity accompanying the scattered line, which is not present in fig. 6.

FIG. 8 shows the same line as scattered by carbon tetrachloride. The nebulosity is not so prominent as in benzene.

FIG. 9 gives the complete spectrum of the mercury arc used for polarisation measurements (for comparison with figs. 10 to 12).

FIG. 10.—Spectrum of the mercury arc scattered by benzene, taken with a nicol in front of the slit of the spectrograph. In (*a*) the shorter axis of the nicol was perpendicular to the track, while in (*b*) it was parallel to the track.

FIG. 11 shows similarly the polarisation of the scattered radiations from carbon tetrachloride.

FIG. 12 is a similar spectrogram of the radiations scattered by amyl alcohol. Note the continuous radiations are also partly polarised.

# *The Thermionic Emission Constant A.*

By R. H. Fowler, F.R.S.

(Received November 20, 1928.)

§ 1. *Summary of Paper.*—The main object of this paper is to apply Nordheim's theory of the emission coefficient of electrons from metals so as to explain the remarkable relation between the constants A and $\chi$ of the thermionic emission formula, first recorded by O. W. Richardson and recently reformulated by Du Bridge. This theory regards the emission as due to the passage of electrons through simple surface potential steps and double layers, to be calculated according to the wave mechanics. We conclude that the theory gives a completely satisfactory account of the facts whenever it can be properly applied. The necessary conditions for its proper application are formulated. Certain apparent discrepancies in absolute magnitude between the observed and theoretical values of A are left outstanding and it is necessary to discuss possible explanations of these in some detail. It is concluded that though their precise cause cannot yet be specified they can certainly be explained and their existence is in no way antagonistic to the main theory.

§ 2. *The Experimental Facts.*—Much attention has been devoted recently to the values of the constant A in the formula for the saturated thermionic (electronic) current I, namely,

$$I = AT^2 e^{-\chi/kT}, \tag{1}$$

where T is the absolute temperature, $\chi$ the work function and $k$ Boltzmann's constant. Particularly interesting measurements of A (and $\chi$) have been recorded by Du Bridge[†] for platinum when very severely outgassed. Du Bridge seems definitely to have established that for really clean platinum the photoelectric threshold and the thermionic work function agree at or near 6·35 volts, and that the corresponding values of A for various specimens range from 10,000 to 20,000 amp./cm.².

Du Bridge also observes that the changes of $\chi$ during the outgassing process are always accompanied by changes of A of such a nature that

$$\log A = \xi + \eta\chi \qquad (\eta > 0), \tag{2}$$

where $\xi$ and $\eta$ are constants, $\eta$ in particular depending on the type of surface dealt with. This relationship has also been pointed out before and in fact examined in some detail experimentally by O. W. Richardson,[†] who has shown that it holds for a variety of metals and surface contaminations.

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[†] Du Bridge, 'Phys. Rev.,' vol. 31, p. 236, and p. 912 (abstract) (1928).

We shall accept these facts as securely established.

§ 3. *Electronic Theory.*—Our present picture of the conduction electrons in a metal which we owe to Pauli and Sommerfeld is, of course, still lacking in refinement. We picture them as moving freely in a region in which their potential energy is negative if their potential energy outside the metal is taken as zero. We ignore the space-variations of this potential which must exist owing to the atomic structure of the metal. The electrons are very tightly packed and must obey the Fermi-Dirac Statistics. They must also have very long free-paths—many hundreds of atoms long in a pure metal. This last characteristic may almost be regarded rather as an experimental fact (apart from all theory) deduced from the nature of the resistance of alloys and metals with small admixtures of impurities. We may question this picture (we will return to possible objections later), but if we accept it, as I am persuaded we must, then we can draw from it perfectly definite rigorous conclusions as to the theoretical formula for I. We conclude that

$$\mathrm{I} = 120\mathrm{D}^* \mathrm{T}^2 e^{-\chi/k\mathrm{T}}, \tag{3}$$

where D* is the mean transmission coefficient of incident electrons (with sufficient energy) through the steep potential gradients at the metal surface.[‡] D* is a mean value over all possible electrons, and consequently may depend on the temperature. The value of $\chi$, the theoretical work function may, of course, depend on the temperature. It cannot yet be theoretically calculated. The theory tells us unambiguously for what types of surface potential curves D* is practically independent of the temperature or violently temperature-dependent. It states further that

$$\mathrm{A} = 120\ \mathrm{D}^*\ \text{amp./cm.}^2,$$

and from the nature of the case[§]

$$\mathrm{D}^* \leqslant 1, \qquad \mathrm{A} \leqslant 120. \tag{4}$$

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[†] (1) Richardson, 'Roy. Soc. Proc.,' A, vol. 91, p. 524 (1915); (2) Richardson and Young, *ibid.*, vol. 107, p. 377 (1925); Young, *ibid.*, vol. 104, p. 611 (1923).

[‡] Fowler, 'Roy. Soc. Proc.,' A, vol. 117, p. 549 (1927); Nordheim (1) 'Z. Physik,' vol. 46, p. 833 (1928) and (2) 'Roy. Soc. Proc.,' A, vol. 121, p. 626 (1928); Fowler and Nordheim, 'Roy. Soc. Proc.,' A, vol. 119, p. 173 (1928).

[§] The theoretical maximum for A has previously been given as 60 by many authors. This is altered to 120 by including the electron's spin.

Provided the work functions have been properly identified there is thus sometimes a grave discrepancy between the observed and calculated values of A.

In attempting to remove this discrepancy one's first instinct is to question the existing electronic theory, but I do not think that, so far as concerns the formula (3), its position can now be shaken. The conception of a Fermi-Dirac gas of "free" electrons, thanks to work by Bloch[†], now in course of publication, undoubtedly leads to such a satisfactory understanding of electrical conduction that it must be accepted as a sound first approximation. The free paths of the electrons inside a pure metal must be long, so that the number of electrons incident on unit area of the surface in unit time can hardly be in doubt and not more than all such incident electrons (with sufficient energy) can escape. This is all that is required to give the inequality (4). Anyone who is still sceptical must remember too that the formula (3) and inequality (4) are equally necessary consequences of any form of electronic lattice theory[‡] in which the metallic electrons can be in equilibrium with the external vapour of electrons. One cannot escape from (4) merely by denying the accepted picture of a metal. This is because one can derive the formula from the properties of the vapour phase and the general laws of statistical equilibrium, which are not necessarily affected by the details of the picture of the metal adopted.

§ 4. *Theories of A.*—Apart from such denials of the whole theory, there are certainly three not impossible ways in which we may avoid the discrepancy between the theoretical values of A and those shown in certain experiments :—

(i) We may assert that the surface conditions are such that $D^*$ varies strongly with the temperature so that part of it is included by the experimentalist's analysis in $e^{-\chi/kT}$. The derived A and $\chi$ are then not comparable with the emission coefficient and the work function.

(ii) We may follow Schottky[§] in asserting that $\chi$ depends on the temperature and really has the form

$$\chi = \chi_0 - \alpha kT.$$

The usual analysis then throws an extra factor $e^{\alpha}$ into A.

(iii) We may assert that the observed areas of emission are wrong.

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[†] Bloch, 'Z. Physik' (in course of publication).

[‡] The electronic lattice must have a specific heat contribution which is practically zero, but we know that this must be so.

[§] Schottky and Rothe, 'Handbuch der Experimentalphysik,' vol. $\text{XIII}_2$, p. 50. The most significant observations seem to be those of Zwikker on hafnium.

These theories we will discuss somewhat further at the end of this paper. It is sufficient to note them here and to conclude that the apparent discrepancies of absolute value are not necessarily insuperable or fatal to the main theory. The main purpose of this note is to show that assuming the absolute values of A can be accounted for, the rest of the existing theory of thermionic emission is extremely satisfactory on account of the beautiful explanation which it gives of the general form of the relation (2).

Nordheim (*loc. cit.* (1)) has given the theory of the emission coefficient D (W) for electrons of kinetic energy W in their motion normal to the surface incident on boundary discontinuities of potential. His formula for D (W) for the boundary potential curve shown in fig. 1 contains an algebraical slip. It may prove of some importance to correct this, for it makes D (W) vanish for W = B whereas really D (W) increases steadily with W from zero at W = C up to and through the value W = B. It will also be worth while to discuss the consequences of his formula (corrected) in greater detail than he did owing to Du Bridge's new material which is now available.

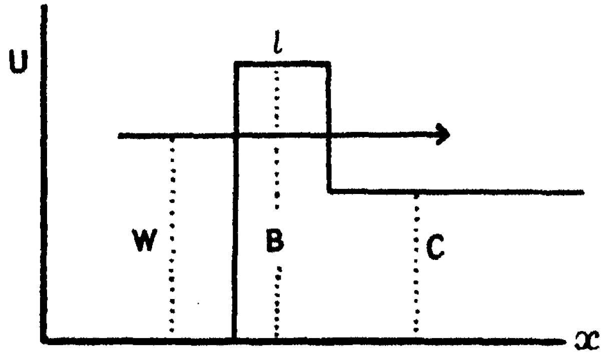

FIG. 1.

The wave-equation for the motion normal to the boundary is

$$\left[\frac{1}{2m}\left(\frac{-ih}{2\pi}\right)^2\frac{\partial^2}{\partial x^2}+\mathrm{U}-\frac{ih}{2\pi}\frac{\partial}{\partial t}\right]\Psi=0,$$

which is of course satisfied by

$$\Psi=\psi e^{-2\pi i\mathrm{W}t/h},$$

where

$$\frac{\partial^2\psi}{\partial x^2}+\kappa^2(\mathrm{W}-\mathrm{U})\,\psi=0\qquad\left(\kappa^2=\frac{8\pi^2m}{h^2}\right).$$

In regions of constant U we take as the general solution

$$\Psi=[ae^{i\kappa(\mathrm{W}-\mathrm{U})^{\frac{1}{2}}x}+a'e^{-i\kappa(\mathrm{W}-\mathrm{U})^{\frac{1}{2}}x}]\,e^{-2\pi i\mathrm{W}t/h}/(\mathrm{W}-\mathrm{U})^{\frac{1}{4}},$$

and if particles or waves are travelling only to the right

$$\Psi = \frac{a}{(\mathrm{W}-\mathrm{U})^{\frac{1}{4}}} \exp\{i\kappa(\mathrm{W}-\mathrm{U})^{\frac{1}{2}} x - 2\pi i \mathrm{W} t/h\}.$$

The value of $|a|^2$ gives, as Nordheim has shown, a measure of the number of electrons in the stream crossing unit area in unit time, and the ratio of $|a|^2$ for the emergent to $|a|^2$ for the incident beam the value of the emission coefficient D (W). If we now work out D (W) for the U of fig. 1, we find

$$\mathrm{D}(\mathrm{W}) = 0 \qquad (\mathrm{W} < \mathrm{C}), \tag{5}$$

$$\mathrm{D}(\mathrm{W}) = \frac{8\{\mathrm{W}-\mathrm{C})/\mathrm{W}\}^{\frac{1}{2}}}{\frac{\mathrm{B}}{\mathrm{W}}\frac{(\mathrm{B}-\mathrm{C})}{(\mathrm{B}-\mathrm{W})}\cosh\{2\kappa(\mathrm{B}-\mathrm{W})^{\frac{1}{2}} l\} + \left\{1 + \left(\frac{\mathrm{W}-\mathrm{C}}{\mathrm{W}}\right)^{\frac{1}{2}}\right\}^2 - \left\{\left(\frac{\mathrm{B}-\mathrm{W}}{\mathrm{W}}\right)^{\frac{1}{2}} - \left(\frac{\mathrm{W}-\mathrm{C}}{\mathrm{B}-\mathrm{W}}\right)^{\frac{1}{2}}\right\}^2} \quad (\mathrm{C} < \mathrm{W} < \mathrm{B}), \tag{6}$$

$$\mathrm{D}(\mathrm{W}) = \frac{8\{(\mathrm{W}-\mathrm{C})/\mathrm{W}\}^{\frac{1}{2}}}{\frac{\mathrm{B}}{\mathrm{W}}\frac{\mathrm{C}-\mathrm{B}}{\mathrm{W}-\mathrm{B}}\cos\{2\kappa(\mathrm{W}-\mathrm{B})^{\frac{1}{2}} l\} + \left\{1 + \left(\frac{\mathrm{W}-\mathrm{C}}{\mathrm{W}}\right)^{\frac{1}{2}}\right\}^2 + \left\{\left(\frac{\mathrm{W}-\mathrm{B}}{\mathrm{W}}\right)^{\frac{1}{2}} + \left(\frac{\mathrm{W}-\mathrm{C}}{\mathrm{W}-\mathrm{B}}\right)^{\frac{1}{2}}\right\}^2} \quad (\mathrm{B} < \mathrm{W}). \tag{7}$$

This is Nordheim's result, with the slip corrected. The general nature of D (W) as a function of (W) is shown in fig. 2. It will be observed on expanding the cosh or cos in (6) and (7) that D (W) is given in both regions by the same uniform analytic function of W, without pole or zero at W = B. In fact

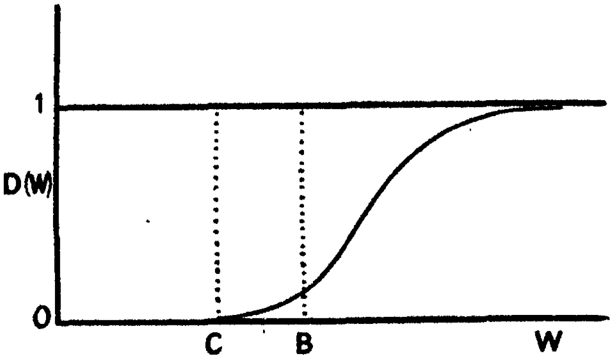

Fig. 2.

$$\mathrm{D}(\mathrm{W}) = \frac{8\{(\mathrm{W}-\mathrm{C})/\mathrm{W}\}^{\frac{1}{2}}}{2\left\{1 + \left(\frac{\mathrm{W}-\mathrm{C}}{\mathrm{W}}\right)^{\frac{1}{2}}\right\}^2 + \frac{\mathrm{B}}{\mathrm{W}}\frac{(\mathrm{B}-\mathrm{C})}{(\mathrm{B}-\mathrm{W})}\sum_{j=1}^{\infty}\frac{\{4\kappa^2 l^2(\mathrm{B}-\mathrm{W})\}^j}{2j\,!}} \quad (\mathrm{W} > \mathrm{C}).$$

Nordheim's discussion suggests further that if the potential gradients at the sides of the hump are still steep but the top is not flat, the term

$$\kappa l\,(\mathrm{B}-\mathrm{W})^{\frac{1}{2}}$$

can probably be replaced with reasonable accuracy by

$$\kappa \int_0^l (\mathrm{U}-\mathrm{W})^{\frac{1}{2}}\,dx,$$

at least when it is large. The square-shouldered hump of fig. 1 cannot, of course, really represent the boundary potential energy step, which must fall somehow from B to C in a short distance $l$, and include the image effect.

When we know D (W) we can at once deduce D* with sufficient accuracy from the equation, given by Nordheim

$$\mathrm{D}^* = \int_0^\infty \mathrm{D}\,(\mathrm{C}+k\mathrm{T}x)\,e^{-x}\,dx. \tag{8}$$

More than one type of behaviour of D* is now possible, depending on the relative sizes of $e^{-(\mathrm{B}-\mathrm{C})/k\mathrm{T}}$ and $e^{-2\kappa l(\mathrm{B}-\mathrm{C})^{\frac{1}{2}}}$. For values of W greater than or equal to B, D (W) can be assumed without serious error to be of order unity. The contributions to D* from this region of the integral are therefore of order $e^{-(\mathrm{B}-\mathrm{C})/k\mathrm{T}}$. When $\mathrm{W}=\mathrm{C}+\varepsilon$, $\varepsilon$ small, we have with sufficient accuracy

$$\mathrm{D}\,(\mathrm{W}) \backsim \frac{16\,(\varepsilon\mathrm{C})^{\frac{1}{2}}}{\mathrm{B}}\,e^{-2\kappa l\,(\mathrm{B}-\mathrm{C})^{\frac{1}{2}}},$$

and this is the order of these contributions to the integral. It is obviously only when these contributions are dominant that we can hope to get a D* which does not depend seriously on the temperature. We then find more exactly from (8)

$$\mathrm{D}^* = \frac{16}{\mathrm{B}\,(\mathrm{B}-\mathrm{C})}\int_0^{(\mathrm{B}-\mathrm{C})/k\mathrm{T}} \{k\mathrm{T}x\,(\mathrm{C}+k\mathrm{T}x)\}^{\frac{1}{2}}\,(\mathrm{B}-\mathrm{C}-k\mathrm{T}x)\,e^{-2\kappa l(\mathrm{B}-\mathrm{C}-k\mathrm{T}x)^{\frac{1}{2}}-x}\,dx + \mathrm{O}\,\{e^{-(\mathrm{B}-\mathrm{C})/k\mathrm{T}}\}. \tag{8'}$$

This approximation to D (W) is only valid because the contributions to the integral near W = B are trivial, for in this region the approximation itself fails. Approximation to the integral can be made in the obvious way and we obtain the result that if

$$e^{-(\mathrm{B}-\mathrm{C})/k\mathrm{T}} \lll e^{-2\kappa l\,(\mathrm{B}-\mathrm{C})^{\frac{1}{2}}}, \tag{9}$$

$$\mathrm{D}^* \backsim 8\sqrt{\pi}\,\frac{(k\mathrm{TC})^{\frac{1}{2}}}{\mathrm{B}}\,e^{-2\kappa l(\mathrm{B}-\mathrm{C})^{\frac{1}{2}}}. \tag{10}$$

This temperature dependence is trivial. If the observed thermionic emission can be fitted to a formula with a constant A and a $\chi$ equal to the true photoelectric threshold, the theory requires therefore that (9) shall hold and that $D^*$ shall be given by (10), or some similar formula modified to take account of the variation of the potential through the hump. When $B = C$ the value of $D^*$ given by Nordheim *loc. cit.* (1) is $2(\pi k T/C)^{\frac{1}{2}}$. The value given by the asymptotic formula (10) is then four times too large, but actually such a value is close to the true value when the image field is allowed for.† For the qualitative discussion which alone is possible we may use (10) as an exact formula. It leads to

$$\log A = \xi - 2\kappa (B - C)^{\frac{1}{2}} l, \tag{11}$$

or more generally

$$\log A = \xi - 2\kappa \int_0^l (U - C)^{\frac{1}{2}} dx. \tag{12}$$

Since $B - C$ is the *decrease* in $\chi$ due to the surface layer we may write (2) in the form

$$\log A = \xi - \eta (B - C). \tag{13}$$

It is fair to claim therefore that (11) or (12) give a completely satisfactory account of the observed (13). Experimental determinations of A are necessarily rough, and a variation of log A with some power of $\chi$ other than unity (but close to it) are not excluded. Moreover (11) or (12) will certainly vary with $\chi$ more rapidly than the power $\frac{1}{2}$, for the thickness $l$ of the double layer must increase with the change in $\chi$. Turning to numerical values, Du Bridge gives exact figures only for platinum, and even there it is not clear that his figures all refer to the same specimen. But a fair representation of his results for platinum treated in his manner is the equation

$$\log_{10} A = 4{\cdot}11 - 1{\cdot}8\, \Delta\chi \quad (\Delta\chi \text{ in volts}).$$

The condition (9) is satisfied, for, when $\Delta\chi = 1$

$$e^{-2\kappa l (B-C)^{\frac{1}{2}}} = 10^{-1{\cdot}8}, \quad e^{-(B-C)/kT} = 10^{-3{\cdot}3}.$$

On comparing this with (11) the variable term agrees if, for $\Delta\chi = 1$, we have $= 10^{-7}$ cm.—that is a rather thick surface layer, but the value is entirely reasonable. Du Bridge points out that the coefficient of $\Delta\chi$ varies fairly widely for different surfaces, being rather small for coated tungsten surfaces and large for liquids. These variations are naturally covered by the theory, the double layer for a given $\Delta\chi$ being thin for tungsten and thick for the liquids studied. The effect of surface layers on tungsten has already been explained in this way by Nordheim, who showed that for tungsten they were monomolecular, but when his paper was written the importance of formula (13) was not realised. Similar relationships for platinum and tungsten contaminated with gas films were given by Richardson (*loc. cit.* (1)), but we shall be content to analyse numerically only the more recent results. A similar relationship has been found for potassium contaminated with hydrogen or water vapour (Richardson, *loc. cit.* (2)) to which we devote § 6. Apart from the absolute value of A in certain cases it therefore seems fair to conclude that the theory gives a most satisfying account of the whole range of thermionic emissions by clean surfaces, or surfaces so contaminated that the true work function is diminished. Before claiming that any particular data should be covered by the theory it must be shown that the emission is properly expressible in the standard form (1) over a wide temperature range, and that the work function and the photoelectric threshold agree. The explanation of the variations of A with surface film offered by the wave-mechanics is of exactly the same nature as the beautiful explanation of the Geiger-Nuttall law of $\alpha$-ray radioactive disintegrations worked out by Gamow.[†]

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† Nordheim, *loc. cit.* (2).

§ 5. *Further Discussion of the Theories of A.*—(i) Abnormal values of A and $\chi$ will certainly be found if $D^*$ varies strongly with the temperature. We have shown that condition (9) must be satisfied before a temperature-independent $D^*$ can be obtained. In the opposite extreme when

$$e^{-(B-C)/kT} \gg e^{-2\kappa l(B-C)^{\frac{1}{2}}}, \tag{14}$$

so that the potential hump is wide and correspondingly powerful, we find easily that $D^*$ behaves like

$$A' e^{-(B-C)/kT}.$$

The metal will then really emit electrons very much as if it had an apparent work function $\chi + B - C$ instead of the true $\chi$. Thermionic analysis would present it with the large $\chi$ and a normal $D^*$ instead of with the true $\chi$ and a very small temperature-dependent $D^*$. Theoretically the true $\chi$ could still be determined photoelectrically; it is, however, doubtful if such a distinction could actually be established, for in the conditions contemplated the values of D (W) for values of W less than B are extremely small. The number of photoelectrons per given number of incident quanta is at best extremely small near the threshold, and if this number is still further cut down by the factor D (W) the photoelectric current in this region might well be undetected, and the apparent threshold agree with $\chi + B - C$. The point to be remembered is that even if the photoelectric threshold is measured and agrees with the apparent work function, it is not necessarily true that the genuine work function has then been determined. Such difficulties, however, are not to be expected for surfaces which are clean or contaminated with simple fairly thin double layers. If, however, the threshold and the work function do not agree closely in any experiment, the results of that experiment certainly cannot be used in the usual simple study of the emission coefficient based on equation (1).

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[†] Gamow, 'Z. Physik,' vol. 51, p. 204 (1928).

Between the two extremes first noted there is room for a large variety of behaviour in $D^*$, even as given by the simplified equation (8′). It may be (see § 6) that this behaviour can account for emissions observed from more complicated surface layers, especially such as do not allow of a good representation by means of equation (1) with A and $\chi$ constant. Such an explanation, however, is not admissible for Du Bridge's results for clean platinum, for which A and $\chi$ are good constants, the surface conditions as simple as possible, and the work function and threshold in close agreement. It is further not possible to explain Kingdon's[†] results for oxygen films on tungsten in this way. Kingdon obtains an emission which can be represented by formula (1) with $A = 5 \times 10^{11}$, $\chi = 9 \cdot 2$ volts. Before contamination with oxygen the tungsten was clean and normal, with $A = 60$, $\chi = 4 \cdot 5$. It is impossible to believe here that $\chi$ is a true work function and A an emission coefficient. It is much more likely that a great part of the whole new factor $10^{10}e^{-4 \cdot 7/kT}$ introduced by the oxygen is really a temperature-dependent emission coefficient, representable in this form over a short temperature range. I have found, however, that it is impossible to make equation (8′) for $D^*$ simulate any such formula with constant values of $l$ and $B - C$. On the other hand it can easily reproduce such a variation if $l$ and (or) $B - C$ are temperature-dependent. Such assumptions, however, are of much the same nature as Schottky's that $\chi$ itself is temperature-dependent and will not be pursued further. The variety of possible uncontrollable hypotheses (if such assumptions are admitted) becomes too large for profitable discussion. It is right to observe, however, that Kingdon had to take his measurements while a continual supply of oxygen was maintained—otherwise the oxygen film would not remain complete. This means that at the high temperatures of the observations there is a considerable rate of escape of the oxygen from the layer, which rate will necessarily vary rapidly with the temperature. The properties of the surface layer are therefore certainly temperature-dependent in this experiment and the results are not significant for any theory of emission through given surface double layers. The same dependence of the surface layer itself on the temperature may well have obtained in those of the experiments of Richardson and Young in which their emission formulæ depended sensibly on the gas pressure.

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[†] Kingdon, 'Phys. Rev.,' vol. 24, p. 510 (1924).

(ii) Schottky's suggestion that $\chi = \chi_0 - \alpha k\mathrm{T}$ is put forward apparently to account for all departures of A from its normal value. In view of the natural explanation which we have found in §4 for the variation of A with $\chi$ for a given metal with a changing contamination the suggestion should probably not be accepted so widely. If $\chi = \chi_0 - \alpha k\mathrm{T}$, and $\alpha$ is to account for the concurrent variations in log A and $\chi_0$, then changes in $\alpha$ must be proportional to changes in $\chi_0$. There is no obvious satisfying reason for such a correlation. The existence of the term $-\alpha k\mathrm{T}$ is, however, a possible explanation of the *absolute* values of A found by Du Bridge for clean and contaminated platinum. This explanation is not ruled out by the agreement of the apparent work function $\chi_0$ and the photoelectric threshold, for $\chi_0$ is the true work function at low temperatures at which the photoelectric effect is usually measured. In Du Bridge's experiments with platinum an extra factor of 120 in A will appear if $\alpha = 4 \cdot 79$. The theoretical threshold at room temperatures (300° K.) will then only differ from $\chi_0$ by 0·12 volts, a not impossible divergence.

As we have already noted, this temperature term in $\chi$ is by no means unacceptable as an explanation or partial explanation of the emission from disintegrating films such as oxygen on tungsten in Kingdon's experiments. It is less agreeable that it should be required for a simple surface of clean platinum, and it is desirable to try to locate its origin. If we accept Sommerfeld's picture of a metal, or any picture of that nature, the work function $\chi$ appears as†

$$\chi = \chi' - \varepsilon^*$$

where $\chi'$ is the potential step at the boundary, and $\varepsilon^*$ a modification of the thermodynamic partial potential of the electrons. It is true that $\varepsilon^*$ must depend on the temperature. According to Sommerfeld's theory $\varepsilon^*$ has approximately the value

$$\varepsilon^* = \frac{h^2}{8m}\left(\frac{3\bar{n}}{\pi}\right)^{2/3} - \frac{\pi^2}{12}\,\frac{8m}{h^2}\left(\frac{\pi}{3\bar{n}}\right)^{2/3} k^2\mathrm{T}^2.$$

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† See for example, Fowler, 'Roy. Soc. Proc.,' A, vol. 117, p. 549, and vol. 118, p. 229 (1928). The weight $g$ of a free "electron" there retained has here been given its value 2.

In this formula $\bar{n}$ is the density of the free electrons in the metal. The second term in $\epsilon^*$ is the value according to this theory of

$$T\int_0^T \frac{dT'}{T'^2}\int_0^{T'} \sigma\, dT'',$$

where $\sigma$ is the specific heat of electricity per electron. We see at once that $\epsilon^*/kT$ gives theoretically a term of the wrong sign to give an increased value of A. It is also far too small. To account for Du Bridge's factor of 120 for platinum we want a factor $e^{4\cdot 8}$ and therefore a term $-4\cdot 8kT$ in $\chi$. If we calculate the extra term in $\epsilon^*$ for $T = 2000°$ K., $\bar{n} = 10^{22}$ (extremely favourable values) we find only $0\cdot 08kT$. If we recall that observed specific heats of electricity at ordinary temperatures may be as much as ten times larger than those of Sommerfeld's theory we are still five times too small. If we take the observed value of the specific heat of electricity for platinum which is *negative* and constant at $9 \times 10^2$ erg per electromagnetic C.G.S. unit from $-50°$ C. to $+100°$ C. and assume that it continues to have this value from 2° K. to 2000° K. we again can only achieve a term $-0\cdot 7kT$ in $\chi$. We therefore cannot assign the origin of Schottky's term to the specific heat of electricity extrapolated without serious change from ordinary temperatures, or in short, to $\epsilon^*$, *so long as the number of free electrons per atom is constant.*

There remain two possibilities, a variation (diminution) of the potential step $\chi'$ at higher temperatures or an increase in the number of free electrons per atom. The order of magnitude of the effect in platinum must be a change of 0·70 volt at 1700° K., produced either by a diminution of $\chi'$, a "loosening" of the lattice, or by an increase in the first term in $\epsilon^*$, or by a combination of the two. The necessary change represents a change of about 5 per cent. in $\chi'$, or of 10 per cent. in $\bar{n}$. These are not impossible. If the change actually occurs mainly in $\bar{n}$ at high temperatures, which seems the more likely, it would have a direct effect on the specific heat of electricity. If observations of this at high temperatures were possible we might obtain an independent control of these hypotheses. At present no control is possible since we have no theory on which to compute the changes of either $\chi'$ or $\bar{n}$.

It should be observed that, while changes in these directions in $\chi'$ and $\bar{n}$ are reasonable and so may be able to account for the observed excessive values of A, changes in the opposite directions (increase of $\chi'$ or decrease in $\bar{n}$ at higher temperatures) are most unlikely so that an explanation in this manner of subnormal values of A cannot be accepted.

(iii) The attractive feature in the third suggestion, that the observed areas are wrong, is provided by the work of Bowden and Rideal[†] on the overpotential of the hydrogen electrode. It must be admitted that it is most unlikely that the effective emitting area of Du Bridge's platinum was really 120 times its apparent area, but none the less the work of Bowden and Rideal merits close attention in the interpretation of thermionic experiments. We cannot discuss their evidence here, but they appear to have shown conclusively that silver may have a true surface (as measured by the hydrogen required to establish a double layer of given strength) 50 times its apparent surface, nickel 45 times and platinised platinum up to 1800 times. In their experiments smooth platinum foil, not heat treated, had an area only twice its apparent area. They showed also that the true surface of nickel could be increased five times by activation (alternate oxidation and reduction in an electric furnace) without change of its appearance under a microscope except a slight loss of brightness.

In Du Bridge's experiments the platinum was violently outgassed. It is necessary to dislodge the contamination (probably hydrogen) in a thickish surface layer, and this treatment inevitably tears up the metal surface. In view of Bowden and Rideal's results and the known power of platinum to form a metal sponge it is not unlikely that the true surface of the platinum emitter is very many times its apparent surface. One might even venture to attribute the whole extra factor in A to this effect if it were not that the greater part of such excessive areas must lie in deep cuttings or almost perfect enclosures into which the applied field which produces an apparently saturated current will not penetrate. Owing to this lack of penetration large factors cannot be obtained in this way, but it is likely that much of the variation in A from specimen to specimen is due to this cause. Variations of this nature in the true emitting area probably occur for all metals, especially soft ones.

§ 6. *Richardson's results for potassium.*—The similar relation between A and $\chi$ observed by Richardson[‡] for clean (or fairly clean) and "sensitised" potassium surfaces takes the form

$$\log_{10} \mathrm{A} = 12 \cdot 4\chi - 15 \cdot 4,$$

(A in amperes/cm.$^2$ and $\chi$ in electron volts). One value of A is recorded in his figure somewhat greater than 120, but all the rest lie below as we should expect. We assume in the discussion that follows that the currents observed are all genuine thermionic currents in spite of their surprisingly low work function. The coefficient of $\Delta\chi$ is large. If the effect is due to a double layer the normal work function for clean potassium should be 1·41 volts, and the double layer required to reduce the work function by 1 volt must be about $7 \times 10^{-7}$ cm. thick. This is not entirely impossible.

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[†] Bowden and Rideal, 'Roy. Soc. Proc.,' A, vol. 120, pp. 59, 80 (1928).

[‡] Richardson, *loc. cit.* (2), p. 393, fig. 6. I am greatly indebted to Prof. Richardson for information about these experiments.

An interesting feature of Richardson's results is the occurrence of emissions which do *not* satisfy equation (1) with constant A and $\chi$. His results on the other hand often seem to approximate to such a formula with very small A and $\chi$ at low temperatures (30° C.) and the same formula with larger A and $\chi$ at higher temperatures (200° C.). This is explained by Richardson on a theory of patches with two thresholds. This theory of patches also accounts for the abnormal difficulty in getting saturation in the thermionic current at low temperatures. The photoelectric threshold has been observed for the same specimens in the same condition and is always greater than the greater value of the apparent work function.

It is interesting to compare with these observations what the theory gives us according to equation (8′) bearing in mind condition (9). For a reduction in $\chi$ of 1 volt

$$e^{-2\kappa l(\mathrm{B}-\mathrm{C})^{\frac{1}{2}}} = 10^{-12\cdot 4}.$$

For a temperature of 300° K.

$$e^{-(\mathrm{B}-\mathrm{C})/k\mathrm{T}} = 10^{-16\cdot 8}.$$

For a temperature of 470° K.

$$e^{-(\mathrm{B}-\mathrm{C})/k\mathrm{T}} = 10^{-10\cdot 7}.$$

In the neighbourhood therefore of 300° K. condition (9) is satisfied. We should obtain a normal emission satisfying (1) with the true value of $\chi$ for this surface condition and a very small value of A. In the neighbourhood of 470° K. condition (14) is satisfied (or almost satisfied—it would be properly satisfied at somewhat higher temperatures), and we should just be reaching a condition in which the emission again fits the equation (1) with a normal value of A and a value of $\chi$ too large by B — C. In the intermediate region we get a steady change over from one type of emission to the other. This is almost exactly what Richardson observes, except perhaps that his curves straighten out before A has quite reached its normal value and when $\chi + \mathrm{B} - \mathrm{C}$ is still somewhat less than the $\chi$ for a clean surface, a detail which must not be over emphasised at this stage.

According to this theory, as well as Richardson's patch theory, the photoelectric threshold which will be recorded depends essentially on the nature of the experiments, especially on the sensitivity of the current measurements. The fact that the recorded thresholds are higher even than the higher value of the apparent work function may merely mean that the emission at frequencies below a threshold comparable with the work function for a really clean surface is too weak to be recorded.

There is thus a noteworthy agreement between the theory of this paper and the observed form of the emission observed by Richardson for potassium—a form which can therefore be accounted for without the patch theory. This must not be taken to imply that the surface is not patchy. The saturation phenomena seem still to require the patch theory, and the existence of patches with different surface layers is extremely probable. They may not, however, play the part which Richardson assigns to them. The phenomena are very complicated and now that the theory has been somewhat further developed a re-examination may well be desirable.

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# *Tribo-Electricity and Friction.* IV.—*Electricity due to Air-Blown Particles.*

By Prof. P. E. Shaw, M.A., D.Sc., University College, Nottingham.

(Communicated by Sir William Hardy, F.R.S.—Received August 1, 1928.)

Electric charges due to mutual impact of dust or other particles arise in various ways: (*a*) electric dust- or sand-storms in the Tropics; (*b*) electric snow storms in the Antarctic; (*c*) electric flashes seen in the ejectamenta from volcanoes; and (*d*) electric charges, and possibly sparking, brought about by the raising of organic powders in certain industrial processes.

In this group of effects, charges are produced by the impact of a multitude of *like* particles. Now, frictional- and impact-charges have ever been regarded as resulting from the shock of two *unlike* substances. Until recently there was no principle by which charges from "like" substances could be interpreted; but experiments made by the writer* throw light on the subject by showing that *identical* solid surfaces can charge one another by friction or impact, and, further, that this property of the surfaces changes as rubbing continues. It was there shown that such organic insulators as ebonite and celluloid yield considerable charges, whereas hard inorganic materials such as quartz, calcite and glass, produce smaller effects. When the "like" solids meet in violent impact, not rubbing, the combined net charge is not nil, as might be expected according to Faraday's law of equal and opposite frictional charges, but finite, generally negative; so that the air surrounding the surfaces must attain an equal positive charge.

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* 'Nature,' vol. 118, p. 659 (1926); 'Proc. Phys. Soc.,' vol. 39, p. 449 (1927).

These results, which are extended by the present experiments, suggest a key to the group of effects mentioned at the head of this article.

Laboratory experiments to investigate the effect of flying powders have been made by W. A. D. Rudge and later by G. B. Deodhar* by blowing powders out of a chamber and observing the charges on the effluent qualitatively. They have shown that, after clashing, some powders have a net negative, others net positive, charge; also that the total charge, which is extraordinarily large when fine powder is used, varies inversely as the size of powder used.

It is now desired to go further and ascertain quantitatively the amount of charge on the particles; whether they are all charged positive or all negative; and the nature and amount of charge given to the air which blows them about.

### *Apparatus.*

The apparatus now used is designed to eliminate from the experiment all but one, or at most two, specified materials, so as to imitate the natural phenomena, where the surfaces brought into contact are "like" surfaces. The particles used are metal filings, or sand, or ice.

Fig. 1 is a side elevation. A is a copper cylinder, about 20 cm. diameter

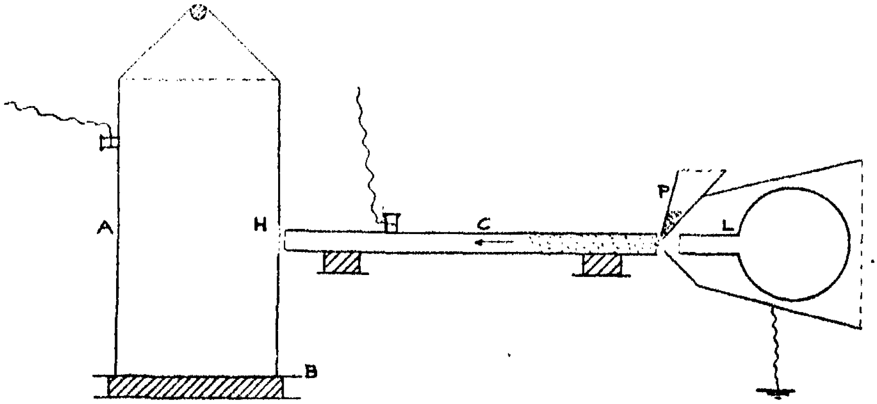

FIG. 1.

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* Rudge, 'Roy. Soc. Proc.,' A, vol. 90, pp. 256, 571 (1914); Deodhar, 'Proc. Phys. Soc.,' vol. 39, p. 243 (1927).

and 40 cm. long, open at each end and having a hole H in the middle of the length through which the particles are blown. B is a metal plate which can be brought under A to close its lower end. C is a copper tube about 3 cm. diameter and 60 cm. long.

A conical hopper P of copper sheet delivers the filings used into the air stream from the motor blower L, which gives a steady hot or cold blast of air. Hopper and blower are screened from the rest of the apparatus by an earthed metal sheet. The filings are measured into a small metal cup, the filler. This is emptied into the hopper.

The electroscope used is of the Hankel type and the parallel field plates are charged to +60 volts and −60 volts. The gold leaf of the electroscope is joined, not to an inductor as in Papers I, II, III of this series,* but directly to the vessels A and/or C, which receive charges due to the impact of filings on them, and which are surrounded by earthed screens in the normal way. The leaf and field plates are adjusted till the sensitiveness is such that 1 volt on the leaf gives 1 division deflection, right or left respectively, on the eyepiece scale of the reading microscope.

### *Experiments.*

These consist of six parts :—

(*a*) Filings leaving the hopper may become charged by it. To test this point, remove A, B and C and the blower. Take a volume $u$ of filings and allow them to fall into the hopper and from it to an insulated plate joined to the electroscope. This volume of filings is used in all subsequent work. Read the resulting potential $v'$. Then allow the same volume of filings to fall direct from the filler to the insulated plate. If the potential is now $v''$, the effect due to the hopper is

$$v_a = v' - v''.$$

Calling the capacity of the plate and electroscope $C_p$ the charge on the filings leaving the hopper is

$$q' = v_a \,.\, C_p.$$

This charge is given to the filings in subsequent work and must be deducted to give us the true charges due to impact. $q'$ is only $+0{\cdot}02$ E.S.U. for Cu and Zn filings, and $+0{\cdot}01$ for Fe and Brass filings.

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* 'Roy. Soc. Proc.,' A, vol. 111, p. 339 (1927) and vol. 118, pp. 97, 108 (1928).

(*b*) B and C being still removed, place the blower about 1 inch from the hole H in A and interpose the lower end of the hopper in the gap thus provided. A volume $u$ of filings is fed into the hopper and these in falling from it are caught by the air stream from the blower and projected across A to strike its wall on the far side. A becomes charged by the impact and the filings, also charged, fall on an earthed plate placed below and beyond A and there give up their charge. The electroscope shows the potential of A. Call it $v_b$. If the capacity of A and electroscope be $C_A$, the charge on A is

$$p_1 = v_b \,.\, C_A - q'.$$

(*c*) Replace B in contact with A and repeat the above operation. The potential of A and B ($v_c$) is due to the algebraic sum of the charge $p_1$ on A and $q_1$ on the filings, all due to the filings striking A, together with charges, if any, arising when the filings fall on B.

(*d*) To find these charges arising when the filings fall on B, allow filings to fall on an insulated plate, the air blast being cut off. If the potential of the plate is $v_d$ and the corresponding capacity $C_t$, and if the plate receive charge $p''$ and the filings charge $q''$ due to the impact

$$p'' + q'' = v_d \,.\, C_t - q'.$$

Trial shows that the impact in this case is so slight that the charge $(p'' + q'')$ is negligibly small and may be ignored in the full equation for (*c*) above:

$$(p_1 + q_1) + (p'' + q'') = v_c \,.\, C_{AB} - q'$$

where $C_{AB}$ is the capacity of A and B and the electroscope. To return to the charges $p_1$ and $q_1$. These are always of opposite sign but, in general, are unequal in amount. It follows that a charge equal and opposite to the sum $(p_1 + q_1)$ is given to the air, since

$$p_1 + q_1 + r_1 = 0.$$

The air charge $r_1$ is carried out of the system by the air blast and is lost.

The above four experiments provide us with values of $p_1$, $q_1$, $r_1$.

(*e*) Keeping A and B in contact, place the left end of C flush with the hole H in A, and set the blower at the right end of C with a space for the hopper as in fig. 1. Join A, B and C to the electroscope. Carry out the experiment with filings as before. They are driven along inside

C. There are two causes, other than mere chance, which tend to bring the filings into contact with the tube. First, the air entering a wide tube like C will have, not a stream-line, but a very turbulent motion, and the various particles will in turn be thrown against the tube. Second, as already shown, the filings enter the tube charged so that, by mutual repulsion, they tend to move outwards from the axis to the wall of the tube. As a result of the many impacts caused both tube and filings attain charges. Let them be $p_2$ and $q_2$ respectively.

On leaving C the filings strike the far side of A and fresh charges $p_1$, $q_1$ on A and filings arise as in (*c*) above. Finally the filings fall on B. Thus if the potential of the system A, B and C is now $v_e$, and the capacity $C_{ABC}$, the total charge is

$$(p_2 + q_2) + (p_1 + q_1) = v_e \,.\, C_{ABC} - q'.$$

(*f*) Lastly, remove A and B, and place an earthed metal plate to receive the filings which fall after leaving C. If the potential of C be $v_f$ and capacity $C_C$ its charge is

$$p_2 = v_f \,.\, C_C - q'.$$

If $r_2$ is the air charge caused by impact in the tube and carried away by the blast, we have,

$$p_2 + q_2 + r_2 = 0.$$

The equations of the last two sections yield the values of $p_2$, $q_2$, $r_2$, since we already know $(p_1 + q_1)$.

The supposition made above is that every contact, whether gentle or violent, between two solid bodies gives rise to charges on each of them and on the air in contact with them. We have assumed this effect as above in four distinct ways; first, when filings pass through a metal hopper; second, when they brush through a tube at great speed; third, when they meet a metal plate at speed; and, lastly, in falling freely, under gravity, a small distance on to a metal plate. In all cases the charges are measurable, though in the last one the charges on filings and plate can be ignored since they enter the equations together and are equal and opposite.

Potential in volts is the actual quantity measured in each case. Then, by comparing the capacity of each part of the apparatus with a standard of 10 cm., the charges are found in E.S.U., as usual, by multiplying potential by capacity and dividing by 300.

Table of Results.

| | $p_1$. | $q_1$. | $r_1$. | $p_2$. | $q_2$. | $r_2$. |
|---|---|---|---|---|---|---|
| Cu/Cu | +0·04 | −0·17 | +0·13 | +0·09 | −0·15 | +0·06 |
| Fe/Cu | +0·03 | −0·07 | +0·04 | +0·05 | −0·02 | −0·03 |
| Brass/Cu | −0·15 | +0·21 | −0·06 | −0·07 | +0·06 | +0·01 |
| Zn/Cu | −0·27 | +0·36 | −0·09 | −0·27 | +0·27 | 0 |
| Cu/Zn | +0·98 | −1·06 | +0·08 | +0·79 | −0·80 | +0·01 |
| Fe/Zn | +0·80 | −0·78 | −0·02 | +0·83 | −0·79 | −0·04 |
| Brass/Zn | +0·42 | −0·37 | −0·05 | +0·38 | −0·37 | −0·01 |
| Zn/Zn | +0·14 | +0·05 | −0·19 | +0·13 | +0·01 | −0·14 |
| Brass/Brass | −0·05 | +0·04 | +0·01 | +0·01 | −0·01 | 0 |
| Sand/Sand (cold blast) | +2·22 | −1·98 | −0·24 | +4·11 | −4·02 | −0·09 |
| Sand/Sand (hot blast) | +5·19 | −8·67 | +3·48 | +9·39 | −8·61 | −0·78 |

The charges $p$, $q$, $r$ in E.S.U., arise on vessel, particles and air, respectively. In the first column, the first material denotes the particles, and the second the sheet material, used. The particles are of size to pass easily through gauze of 0·35 mm. mesh. The volume of one charge of particles is 0·15 c.c. Speed of blast is 54 mls./hr.

It is to be noticed that the whole apparatus is lined with *one material only* ; in the first four lines, with copper ; in the second four, with zinc ; in the ninth line with brass and in the last lines with sand-paper.

We observe in the first eight lines certain systematic relations between the results :—

(1) Values of $p_1$ and $p_2$ decrease progressively positive to negative from Cu to Zn. This applies whether the system be Cu or Zn.

(2) Values of $q_1$ and $q_2$ increase in similar manner. Fig. 2 shows these relations for $p_1$ and $q_1$.

(3) Values of $r_1$ and $r_2$ decrease in a similar way ; in two cases only in the last column there is a slight departure (within the range of experimental error) from regular progression.

(4) The *air* charges, $r_1$, $r_2$, are in general much smaller than those on the *solid* particles and surfaces. Noteworthy exceptions to this rule are seen when *like* metals, Cu/Cu and Zn/Zn, clash.

The regularity of these progressions proves the dependability of the present method. It might be considered strange that charges should be observed between metals in the present impact method, seeing that charges are never found in the usual tribo-electric or impact experiments between two metals. There are, however, in this method certain conditions favourable to the demonstration of charges, as follows: (*a*) Small particles have large area, and therefore capacity relative to their mass, but the contact potential between the two metals is constant, so the quantity of electricity arising is large for a given mass. When a large number of particles are used, as here, the total accumulated charge is relatively large. (*b*) With the great speeds used, the duration of contact is short, and recombination of charges when the surfaces separate is reduced accordingly. (*c*) The electroscope is more sensitive than is usual in tribo-electric experiments.

Recent research already quoted shows that identical insulators can charge one another. In the present experiments we see how identical metals Cu/Cu, Zn/Zn, Brass/Brass behave in the same way, an even more remarkable effect than for insulators.

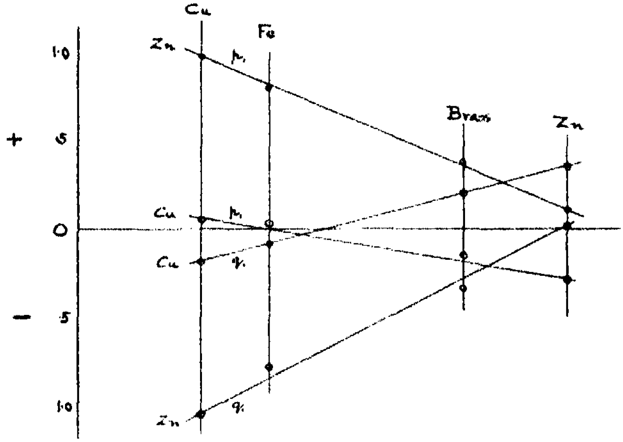

FIG. 2.

In the table above are two sets of results for Sand/Sand. The hopper and the whole inside of the apparatus are lined with fine sandpaper. Here, as in a desert sand-storm, we have no materials operating but sand and air, moving at speed over a sand-strewn ground; and where, as in the second case, the air blast and all sand surfaces are hot we closely approximate to the conditions in a Sirocco. The charges obtained with sand are larger than with metals. This is to be expected, especially at the higher temperature, as insulation is better. The charge found on the sand after merely passing through the hopper was found to be —0·2 E.S.U.

### *Variations.*

The effect of changing various conditions was tried :—

(*a*) *Cleanliness.*—Filings should be made, and all inferior surfaces cleaned, just before use; old filings yield as much as 30 per cent. less charge than new ones. No doubt with lapse of time the clean surfaces attain films of oxide and adsorbed vapours from the air. A similar time-effect on friction has been shown. ('Roy. Soc. Proc.,' A, vol. 118, pp. 348 and 349 (1928)).

(*b*) When *temperature* of the blast changes from 18° to 58°, the charges were doubled in the only cases tried, Copper/Brass, Sand/Sand. The air charges $r_1$, $r_2$, in the latter case increased ten-fold, as the table shows.

(*c*) Reducing the *speed* of the blast from the normal 54 mls./hr. is found to reduce the charges. As in all tribo-electric experiments rapidity in moving the clashing surfaces makes for large charges. In the case of a hot sand blast the charges are reduced 15 per cent. by reducing speed from 54 to 28 miles an hour. At speeds less than the latter, the filings begin to " silt " in the tube.

(*d*) If the air blast be directed not, as usual, along the axis of tube C but *obliquely* against its wall, the charges are found to increase about 20 per cent.

These facts show the necessity of stating the conditions as regards these four factors, if results are to be of standard value.

In addition to experiments on metals and sand, investigations were made on ice; but it is a difficult material to use. The electric snow storms recorded by Dr. G. C. Simpson in Antarctica are found when snow at very low temperature, say, —50° C., is blown at high speed, say, 60 mls./hr. over a snow field. These conditions can be attained in laboratory experiments, but the low temperature cannot easily be maintained for long. I formed ice on a tube of paper by dipping it alternately in water and liquid air. The ice particles are formed by grinding, in a cold mortar, lumps of ice which have been immersed in liquid air for a period. Provided the particles and tube are not kept long in the air after being at —180° C. their temperature will be at some *low* temperature below 0° C.

A blast of cold air is used to blow the particles through the tube and the charge on the tube, insulated and surrounded by an *inductor* connected to the electroscope, is measured as usual. I found high charges, of the order of those in the sand experiments. This demonstrates the electric separation due to impact of ice on ice. To establish the point, two ebonite rods were covered with low-temperature ice (as above) at one end, and with glass handles at the other. When the ice surfaces are rubbed or lightly struck together they are found to be very brittle but with care the "rubber" surface is found to be negative, and the "rubbed" positive. Again, this cold ice is found to be positive to ebonite, sealing wax, amberite and even vitreous silica and mica; so cold ice must be one of the most electro-positive solids known.

If the two ice surfaces are anywhere near 0° C. no tribo-electric charges can be obtained *from them; here impact or friction causes them merely to melt at the place of contact in the usual way. It is doubtless for this reason that snow storms in temperate regions of the earth are not accompanied by electric discharges.*

### *Theory.*

As the table of results shows, the metals Cu, Fe, Brass, Zn, always receive charges of sign, and in some degree of amount, in accordance with a group of well-established effects; the Volta-effect, photo-electric-effect and thermionic-effect. This is a confirmation as far as it goes of Helmholtz's theory that tribo-electric charges arise *for metals*, like the Volta-effect, simply from contact difference of potential. But the three "like" metal cases, Cu/Cu, Zn/Zn and Brass/Brass, as well as the cases Sand/Sand and Ice/Ice show that the Volta-effect alone, as ordinarily understood, will not account for all the charges arising; for here we have the contact of surfaces chemically identical. We are therefore driven to postulate physical differences of the surface, *i.e.*, strain differences, as contributory factors to tribo-electric charges. Permanent strain of the superficial layers of a solid surface occurs when another solid presses (even lightly) on it. The force which tears the particles from a block when it is filed may or may not leave strain in parts of their surfaces. If the heat due to rupture is sufficient to raise the metal to annealing temperature, say, 250° C., the filings may be annealed and free of strain; if not, there must be strain. Again, the sheet metal which the filings strike has some strain caused by cleansing with sand-paper. The subject of superficial strain and the change in electrical properties due to it calls for investigation.

I am glad to acknowledge the help of Mr. R. F. Hanstock and Mr. J. E. Keyston in the observations.

## *Summary.*

(1) The impact of two unlike metals, of two like metals, or of sand on sand, or ice on ice, is studied by driving wind-blown particles of these materials on to surfaces of *one material only*.

(2) The charges arising on the particles, on the surfaces, and on the issuing air, are separately measured.

(3) Results show that the Volta-effect plays a large part, but not the only part, in the genesis of charges, for,

(4) When the particles and surfaces are chemically identical, considerable charges arise.

(5) The results for sand and ice provide a key to the meteorological effects observed in electric sand-storms and snow-storms.

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# *Intensity Measurements in the Secondary Spectrum of Hydrogen.*—II.

By Dr. W. Kapuscinski and Miss J. G. Eymers.

(Communicated by O. W. Richardson, F.R.S.—Received, August 2, 1928.)

In an earlier publication* Prof. Ornstein and the writers gave intensity measurements of a part (4500-4900 A.) of the secondary spectrum of hydrogen. At Prof. Ornstein's instigation the measurements were later extended to other parts of this spectrum, as such measurements may be valuable for the theoretical investigations of the secondary spectrum and the classification of the lines, about which much uncertainty exists as yet. Only the results of the measurements are given in this paper: the theoretical discussion will be submitted later.

For particulars of the experimental methods, readers are referred to the initial publication.

In order to get a greater intensity of light, a tube of the "end-on" type (fig. 1) was substituted for the one previously used. The spectra were taken with the same grating: lines 0·2 A. apart were distinctly separated. The times of exposure ranged, according to the spectral region, from half a minute

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* 'Roy. Soc. Proc.,' A, vol. 119, p. 83 (1928).

(violet) to five hours (green and red); especially in the green part the photographs were difficult to obtain.

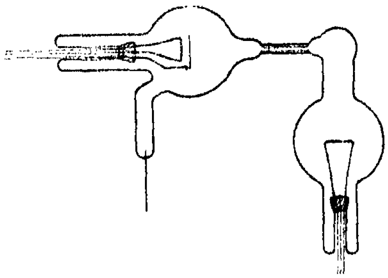

FIG. 1.

The following plates were used:—

| | | |
|---|---|---|
| 3650–4900 A. | Ilford Special Rapid ...... | All "backed." |
| 4900–5660 A. | Astronomical Green ........ | |
| 5660–6450 A. | Panchromatic.............. | |

The whole spectrum was taken at a pressure of hydrogen of about 0·17 mm. (the green part at a slightly higher pressure, 0·21 mm.), and a current of 28–35 m. A. The potential across the electrodes was about 400 volts; a low pressure was used as trials had shown that under these circumstances the discharge best showed the changes in the pressure which invariably occurred. At the conclusion of the experiments the tube was connected to a vacuum pump, and the pressure, at which a discharge similar to that which had been employed, found; it was about 0·20 mm., *i.e.* approximately the same as given above.

By taking several photographs on the same plate, only differing in time of exposure, a good control of the results was possible, for the ratios of the intensities of the lines on each pair of photographs should be constant, consistent with a certain spreading. However, it appeared that on most plates those ratios were in a certain way dependent on the intensity. The following example serves to illustrate this point.

Comparing a dense spectrum with a weak one, it appeared that the ratio for small intensities was systematically greater than the average; with large intensities it was smaller; consequently the smallest intensities were too large and the largest too small. The ratio as a function of the intensity of the denser photograph is as in fig. 2.

The curve cuts the line of the average at intensity 47·5, which means that at intensity 47·5 of the denser photograph the ratio is the right one; consequently, both at intensity 47·5 and intensity 47·5/3·96 = 12, no correction is necessary. An intensity 47·5 for the weaker photograph corresponds to an intensity 47·5 × 5·48 = 260 for the denser one (at 260 the ratio being 5·48). This ought to be 47·5 × 3·96 = 188; therefore it follows that at intensity 260 the correction amounts to — 72.

Similarly, an intensity 3·33 for the weaker photograph corresponds to an intensity 3·33 × 3·60 = 12 for the denser one; as intensity 12 has no correction the intensity 3·33 should be 12/3·96 = 3·03, consequently the correction at 3·33 is — 0·3.

If we make a curve of the correction as a function of the corresponding intensity (fig. 3) by the use of these four points, the part between intensity 47·5 and 12 can be sketched (for we know the correction in that part to be not very great), and with the help of this sketch it becomes possible to find more points. For example, we see from fig. 2 that at intensity 90·8 the ratio to the weaker intensity, 20, is 4·54. Fig. 3 shows us that intensity 20 ought to be 20·4: the ratio being 3·96, the intensity 90·8 must be 20·4 × 3·96 = 80·8. Correction at intensity 90·8 also = — 10. In the same way we can find more points. Moreover, the same plate contained a third denser spectrum. By comparing this one with one of the already-mentioned photographs, we learned that here the correction was 0 at the intensity 48. When this case was treated in the same way as the one just mentioned, an average curve for the correction of the plate was established. On this correction being applied the ratios of corresponding lines in the different photographs are found to be constant, a value approximately the same as if an average had been taken of the initial ratios.

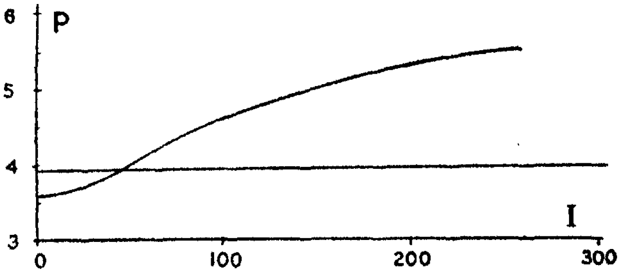

Fig. 2.

The phenomenon is probably due to "developer-effects" which cause the density curves, obtained by means of continuous density marks, to have a slightly too small inclination at high intensities and a slightly too large inclination at lower intensities. Though these effects would have been avoided had " step-weakeners " been used, such a method would cause some difficulties with the astigmatic grating employed, so the method of density marks was preferred.

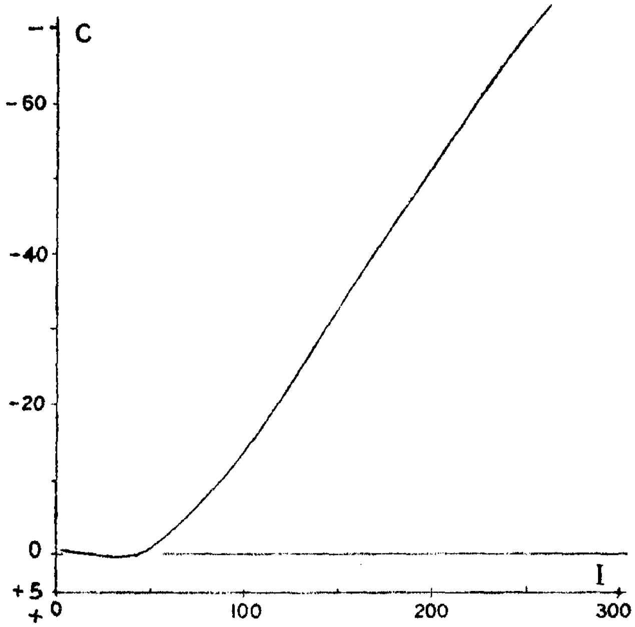

Fig. 3.

The density in the spectra was measured at least twice by means of a Moll registering microphotometer (with first slit). Analyses of doublets or multiplets had to be applied in about 200 cases. Altogether the intensities of 1427 lines were determined. The wave-lengths were taken from the extensive tables of Gale, Monk and Lee,[*] lately published, which gives the best measurements up to date. (It is of interest to note how well the wave-lengths established by the writers for doublets analysed in the previous table agree with these measurements of Gale, Monk and Lee.)

The region 4500–4900 A. was also once more measured, because the pressure differed from that formerly used and because the above-mentioned correction had since been determined and applied.

Finally, an illustration of the accuracy of the measurements are given. The given intensities are those of lines chosen at random from different photographs, all reduced to common terms.

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[†] 'Astrophys. J.,' vol. 67, p. 90 (1928).

Table I.

| Wave-length. | I. | II. | III. | IV. | The average intensity. |
|---|---|---|---|---|---|
| 4505·63 | 36·6 | 33·9 | 33·2 | 34·9 | 34·2 |
| 4686·77 | 92·0 | 88·0 | 87·2 | 78·0 | 88·0 |
| 5317·89 | 16·9 | 14·9 | 15·6 | 16·6 | 16·0 |
| 5474·86 | 28·5 | 28·4 | 33·4 | — | 30·0 |
| 5630·62 | 13·3 | 12·4 | 12·7 | — | 12·8 |
| 6018·29 | 185·0 | 166·0 | 168·0 | — | 173·0 |
| 6399·48 | 47·3 | 47·9 | 51·0 | — | 48·5 |

The weakest and the strongest lines are less accurate, of course, for they could not be measured on all the photographs. Different weight has often been given to the results of the different photographs, owing to the fact that in some cases the lines were very difficult to measure on account of the very large or very low density of the negative.

Table II.

| Wave-length. | Intensity. | Wave-length. | Intensity. | Wave-length. | Intensity. | Wave-length. | Intensity. |
|---|---|---|---|---|---|---|---|
| 3652·46 | 19·5 | 3797·91 | 29·9 | 3867·99 | 10·2 | 3950·57 | 10·8 |
| 55·67 | 12·4 | 99·02 | 34·7 | 69·16 | 26·7 | 51·48 | 10·0 |
| 63·06 | 16·5 | 3800·05 | 10·3 | 69·93 | 42·5 | 55·18 | 10·6 |
| 64·13 | 45·6 | 02·08 | 8·6 | 70·63 | 29·0 | 59·96 | 11·3 |
| 65·24 | 12·3 | 03·03 | 94·5 | 70·91 | 44·3 | 60·19 | 9·5 |
| 65·91 | 48·9 | 03·27 | 14·3 | 71·59 | 154·0 | 62·33 | 27·9 |
| 73·62 | 46·5 | 09·02 | 19·0 | 72·35 | 118·0 | 63·14 | 36·0 |
| 74·40 | 109·0 | 12·17 | 8·4 | 74·12 | 18·5 | 66·80 | 7·3 |
| 80·53 | 9·9 | 12·74 | 23·4 | 77·27 | 7·1 | 68·91 | 7·2 |
| 81·96 | 32·0 | 15·33 | 13·3 | 79·53 | 47·4 | 74·21 | 14·4 |
| 82·29 | 19·0 | 16·79 | 9·7 | 82·05 | 16·7 | 74·77 | 16·0 |
| 84·31 | 119·0 | 24·94 | 20·1 | 84·14 | 39·5 | 75·67 | 23·6 |
| 90·14 | 16·8 | 36·44 | 22·3 | 86·22 | 16·7 | 77·09 | 7·7 |
| 99·78 | 17·8 | 40·55 | 12·2 | 87·39 | 9·8 | 78·15 | 18·1 |
| 3700·05 | 19·9 | 45·83 | 10·5 | 87·84 | 32·6 | 78·67 | 9·6 |
| 02·11 | 42·5 | 46·23 | 19·4 | 88·99+ |  | 79·74 | 10·5 |
| 15·99 | 10·0 | 49·30 | 52·1 | Hζ | 170·0 | 82·63 | 48·6 |
| 22·09 | 27·9 | 49·70 | 15·3 | 89·30 | 112·0 | 83·97 | 36·2 |
| 32·11 | 29·1 | 49·99 | 8·6 | 90·70 | 13·3 | 86·92 | 30·6 |
| 41·21 | 10·0 | 51·27 | 38·4 | 3902·62 | 29·2 | 90·03 | 142·0 |
| 51·88 | 25·2 | 57·78 | 20·8 | 07·48 | 14·4 | 91·15 | 11·4 |
| 70·23 | 11·8 | 58·66 | 37·1 | 10·04 | 8·2 | 91·83 | 89·0 |
| 71·50 | 30·0 | 59·01 | 17·3 | 16·96 | 8·5 | 93·26 | 33·3 |
| 74·30 | 16·0 | 59·88 | 33·7 | 24·41 | 47·5 | 93·85 | 14·6 |
| 75·58 | 12·8 | 60·71 | 63·2 | 27·19 | 6·9 | 96·66 | 11·5 |
| 76·98 | 15·6 | 61·50 | 86·7 | 27·24 |  | 97·14 | 90·5 |
| 90·96 | 11·9 | 63·20 | 75·2 | 28·39 | 9·5 | 98·26 | 8·7 |
| 91·40 | 35·0 | 64·07 | 16·9 | 33·60 | 15·0 | 99·26 | 4·9 |
| 94·46 | 25·6 | 64·27 | 15·5 | 44·27 | 44·2 | 4000·21 | 18·3 |
| 96·60 | 102·0 | 65·49 | 27·6 | 44·82 | 4·8 | 00·84 | 27·9 |
| 97·52 | 72·8 | 67·08 | 51·2 | 46·11 | 8·1 | 02·07 | 6·5 |

Table II—continued.

| Wave-length. | Intensity. | Wave-length. | Intensity. | Wave-length. | Intensity. | Wave-length. | Intensity. |
|---|---|---|---|---|---|---|---|
| 4002·50 | 48·4 | 4061·41 | 3·7 | 4113·52 | 22·5 | 4184·69 | 2·2 |
| 02·98 | 20·1 | 62·46† | 193·0 | 16·31 | 7·4 | 87·73 | 1·6 |
| 05·49 | 65·0* | 63·26 | 10·2 | 23·27 | 2·0 | 88·23 | 8·7 |
| 05·94 | 23·4 | 63·63 | 64·1 | 23·75 | 8·5 | 89·09 | 3·1 |
| 08·72 | 10·1 | 65·62 | 47·0 | 29·54 | 9·4 | 89·46 | 6·2 |
| 09·26 | 6·7 | 66·13 | 21·1 | 30·03 | 3·9 | 92·11 | 5·0 |
| 09·56 | 12·7 | 66·88 | 318·0 | 31·45 | 27·1 | 94·02 | 6·8 |
| 10·74 | 6·3 | 67·16 | 33·7 | 31·95 | 9·0 | 94·31 | 7·4 |
| 13·15 | 13·7 | 69·63 | 395·0 | 32·70 | 2·8 | 95·67 | 156·0 |
| 15·83 | 7·6 | 69·88 | 52·0 | 34·00 | 25·3 | 98·21 | 29·3 |
| 16·31 | 5·2 | 71·24 | 60·9‡ | 38·19 | 2·1 | 98·72 | 2·2 |
| 16·55 | 5·6 | 71·66 | 11·8 | 39·52 | 2·7 | 99·79 | 89·0 |
| 18·90 | 6·6 | 72·96 | 51·0 | 40·82 | 7·6 | 4200·10 | 11·0 |
| 20·93 | 10·8 | 74·10 | 63·8 | 42·04 | 1·6 | 00·97 | 31·2 |
| 21·34 | 21·8 | 74·62 | 4·8 | 42·80 | 5·9 | 02·28 | 13·6‖ |
| 21·79 | 14·5 | 75·01 | 2·9 | 43·29 | 4·6 | 05·10 | 340·0 |
| 23·34 | 3·6 | 75·89 | 1·6 | 43·86 | 4·3 | 06·09 | 36·0 |
| 24·73 | 18·3 | 76·96 | 1·3 | 45·55 | 6·3 | 07·54 | 6·1 |
| 26·22 | 6·6 | 78·17 | 7·8 | 46·24 | 11·9 | 08·23 | 3·7 |
| 26·61 | 10·3 | 78·84 | 151·0 | 46·91 | 3·5 | 08·43 | 5·3 |
| 27·38 | 16·7 | 80·09 | 4·6 | 51·57 | 12·2 | 09·17 | 28·1 |
| 28·33 | 82·5 | 80·46 | 1·3 | 52·16 | 1·6 | 10·13 | 90·8 |
| 30·03 | 2·4 | 80·66 | 2·9 | 52·64 | 5·9 | 11·82 | 7·6 |
| 31·37 | 11·4 | 81·48 | 7·5 | 55·80 | 10·6 | 12·04 | 13·8 |
| 31·76 | 9·8 | 82·38 | 76·2 | 56·62 | 28·9 | 12·50 | 158·0 |
| 32·67 | 3·1 | 83·34 | 2·0 | 56·86 | 31·1 | 14·28 | 6·8 |
| 33·78 | 4·5 | 83·84 | 10·9 | 57·17 | 6·5 | 16·21 | 6·8 |
| 35·57 | 22·6 | 84·01 | 8·3 | 59·30 | 25·8 | 16·67 | 7·8 |
| 38·53 | 4·5 | 84·52 | 5·4 | 61·49 | 6·2 | 19·50 | 9·6 |
| 39·16 | 3·6 | 85·01 | 19·8 | 61·72 | 17·4 | 22·16 | 83·0 |
| 43·11 | 8·4 | 85·24 | 47·5 | 61·94 | 41·2 | 22·52 | 79·0 |
| 43·57 | 61·0 | 87·76 | 197·0 | 62·36 | 2·7 | 23·94 | 50·4 |
| 44·47 | 9·9 | 88·68 | 6·0 | 63·01 | 6·1 | 24·50 | 28·2 |
| 44·77 | 2·9 | 88·91 | 5·4 | 63·39 | 17·2 | 25·55 | 2·0 |
| 45·49 | 5·0 | 89·29 | 4·6 | 63·61 | 35·5 | 26·74 | 5·1 |
| 47·58 | 3·4 | 90·71 | 3·2 | 64·44 | 3·0 | 27·38 | 16·8 |
| 47·95 | 8·0 | 91·07 | 3·4 | 65·20 | 16·1 | 28·81 | 2·4 |
| 48·30 | 23·4 | 91·62 | 3·4 | 66·73 | 1·4 | 31·00 | 3·2 |
| 48·45 | 22·5 | 92·21 | 2·2 | 67·57 | 10·1 | 32·67 | 10·9 |
| 49·18 | 11·4 | 92·81 | 2·1 | 68·57 | 5·9 | 32·89 | 7·6 |
| 51·22 | 14·4 | 93·80 | 3·7 | 71·31 | 137·0 | 33·41 | 30·0 |
| 53·51 | 5·2 | 94·21 | 9·3 | 73·85 | 1·9 | 33·82 | 22·7 |
| 53·99 | 7·6 | 94·75 | 3·3 | 74·05 | 1·4 | 37·55 | 5·0 |
| 54·38 | 3·1 | 95·53 | 24·7 | 75·17 | 88·0 | 43·13 | 6·6 |
| 55·28 | 20·6 | 96·07 | 19·5§ | 77·13 | 375·0 | 43·83 | 23·7 |
| 56·41 | 14·6 | 97·43 | 32·7 | 77·72 | 57·3 | 45·53 | 1·7 |
| 57·15 | 3·4 | 4106·23 | 23·8 | 78·64 | 2·1 | 46·69 | 6·6 |
| 57·55 | 15·5 | 07·79 | 16·8 | 79·60 | 53·5 | 46·99 | 2·8 |
| 58·43 | 2·8 | 09·30 | 20·2 | 80·11 | 124·0 | 53·29 | 19·7 |
| 59·25 | 7·7 | 09·49 | 6·3 | 80·69 | 6·4 | 54·03 | 2·8 |
| 61·09 | 6·4 | 10·12 | 22·5 | 82·17 | 115·0 | 55·22 | 2·4 |
| 61·30 | 4·1 | 11·06 | 9·2 | 84·40 | 2·5 | 56·72 | 3·0 |

* Possibly partially blended by 4005·40.
† Double?
‡ Possibly a little modified by 4071·39.
§ Blend with 4095·95.
‖ Possibly a little influenced by 4202·44.

Table II—continued.

| Wave-length. | Intensity. | Wave-length. | Intensity. | Wave-length. | Intensity. | Wave-length. | Intensity. |
|---|---|---|---|---|---|---|---|
| 4260·34 | 3·6 | 4368·99 | 2·0 | 4422·99 | 15·1 | 4467·75 | 3·0 |
| 61·67 | 2·6 | 70·77 | 5·5 | 23·25 | 21·1 | 68·28 | 4·4 |
| 62·78 | 5·4 | 71·99 | 2·4 | 25·15 | 13·3 | 69·54 | 2·2 |
| 65·16 | 5·2 | 75·54 | 2·0 | 25·90 | 15·2 | 70·72 | 3·7 |
| 67·03 | 1·7 | 79·40 | 20·3 | 26·61 | 3·3 | 71·52 | 12·6‡ |
| 67·91 | 3·8 | 79·96 | 3·5 | 27·75 | 6·3 | 71·96 | 12·6 |
| 72·13 | 2·9* | 81·61 | 1·5 | 28·05 | 2·5 | 74·26 | 24·4 |
| 77·48 | 5·5 | 82·18 | 5·2 | 28·79 | 2·8 | 76·33 | 6·7 |
| 79·42 | 12·6 | 83·03 | 1·7 | 29·30 | 4·4 | 77·07 | 21·6 |
| 80·74 | 6·8 | 83·49 | 12·0 | 31·38 | 6·4 | 77·82 | 3·0 |
| 81·82 | 2·2 | 84·19 | 3·1 | 32·36 | 6·7 | 78·99 | 11·0 |
| 82·71 | 3·0 | 84·46 | 4·8 | 33·88 | 2·7 | 79·39 | 2·7 |
| 86·04 | 3·3 | 86·25 | 4·6 | 34·28 | 5·3 | 79·69 | 4·1 |
| 87·61 | 3·0 | 87·29 | 2·5 | 34·57 | 5·8 | 81·26 | 8·6 |
| 88·85 | 3·3 | 88·89 | 4·3 | 34·99 | 8·7 | 82·08 | 7·0 |
| 89·20 | 2·4 | 89·08 | 13·6 | 35·89 | 4·6 | 82·51 | 3·1 |
| 89·64 | 12·5 | 89·45 | 2·2 | 37·64 | 1·8 | 83·51 | 2·3 |
| 90·11 | 13·6 | 90·90 | 22·5 | 38·21 | 4·5 | 84·16 | 3·2 |
| 90·57 | 3·6 | 91·73 | 7·3 | 38·63 | 8·6 | 86·08 | 41·0 |
| 92·14 | 4·5 | 92·09 | 7·8 | 39·43 | 2·9 | 86·71 | 2·9 |
| 92·70 | 5·4 | 92·89 | 3·1 | 41·40 | 8·6 | 87·81 | 36·2 |
| 94·23 | 3·3 | 94·35 | 3·2 | 41·85 | 2·1 | 88·55 | 3·9 |
| 95·42 | 8·4 | 96·89 | 1·8 | 42·85 | 9·4 | 89·23 | 5·9 |
| 95·64 | 8·3 | 98·08 | 4·1 | 43·46 | 1·8 | 90·45 | 111·0 |
| 98·03 | 2·4 | 98·24 | 6·7 | 44·21 | 18·9 | 93·69 | 36·5 |
| 4303·42 | 56·2 | 98·93 | 1·9 | 45·25 | 72·1 | 95·31 | 3·1 |
| 03·88 | 30·4 | 99·66 | 2·7 | 46·82 | 3·0 | 96·67 | 14·0 |
| 05·82 | 4·5 | 99·95 | 2·2 | 47·55 | 66·7 | 97·10 | 9·0 |
| 06·28 | 35·4 | 4400·75 | 18·7 | 47·93 | 28·3 | 97·58 | 33·0 |
| 07·50 | 3·9 | 00·83 | 3·3 | 49·50 | 4·5 | 98·11 | 61·4 |
| 08·64 | 16·1 | 00·92 | 4·2 | 49·91 | 28·9 | 98·52 | 53·8 |
| 11·70 | 7·1 | 01·41 | 2·8 | 50·35 | 3·2 | 99·55 | 8·6 |
| 12·39 | 4·4 | 01·65 | 2·6 | 50·82 | 15·8 | 4500·05 | 3·5 |
| 12·87 | 11·1 | 02·46 | 2·0 | 51·35 | 4·1 | 01·60 | 3·7 |
| 18·00 | 5·8 | 03·63 | 3·7 | 52·10 | 5·7 | 01·96 | 33·7 |
| 18·22 | 8·9 | 04·17 | 6·7 | 52·77 | 13·9 | 02·74 | 8·9 |
| 20·66 | 2·2 | 04·61 | 19·8 | 53·14 | 19·2 | 04·47 | 13·7 |
| 27·36 | 3·2 | 10·48 | 10·2 | 55·34 | 6·1 | 04·92 | 6·4 |
| 27·93 | 28·2 | 10·62 | 11·6 | 55·67 | 12·3 | 05·63 | 34·2 |
| 29·64 | 2·5 | 12·25 | 86·0 | 55·96 | 8·8 | 09·10 | 3·6 |
| 30·40 | 5·9 | 12·48 | 10·6 | 56·67 | 26·4 | 10·90 | 14·7 |
| 31·38 | 2·8 | 13·50 | 12·8 | 56·85 | 30·9 | 11·33 | 4·3 |
| 32·62 | 19·6 | 14·22 | 33·3 | 57·03 | 9·0 | 11·69 | 31·5 |
| 35·52 | 15·9 | 14·54 | 5·2 | 57·58 | 4·6 | 12·48 | 4·4 |
| 43·60 | 2·6 | 14·99 | 21·5 | 58·30 | 5·9 | 12·87 | 6·9 |
| 46·66 | 1·8 | 16·22 | 12·5 | 58·73 | 20·0 | 13·83 | 9·3 |
| 50·42 | 1·6 | 16·48 | 7·1 | 58·86 |  | 14·31 | 4·6 |
| 50·72 | 2·5 | 17·34 | 47·0 | 59·12 | 13·0 | 15·18 | 7·6 |
| 52·12 | 1·7 | 18·67 | 7·5 | 59·46 | 3·9 | 15·56 | 4·4 |
| 53·41 | 5·8 | 19·49 | 35·4 | 60·19 | 2·0 | 17·43 | 9·6 |
| 54·54 | 10·3 | 19·82 | 6·4 | 60·97 | 90·0 | 17·72 | 3·8 |
| 55·79 | 2·0 | 20·30 | 32·9 | 61·91 | 2·9 | 17·90 | 6·7 |
| 61·92 | 2·8 | 20·92 | 7·4 | 63·88 | 3·5 | 18·13 | 3·9 |
| 67·73 | 6·8 | 21·16 | 8·7 | 64·22 | 8·6 | 19·12 | 10·7 |
| 68·49 | 4·2 | 22·77 | 11·9† | 67·15 | 70·9 | 19·96 | 6·8 |

* Not present in the Tables of Gale, Monk and Lee.

† A partial blend with 4422·65.

‡ A partial blend with 4471·61.

Table II—continued.

| Wave-length. | Intensity. | Wave-length. | Intensity. | Wave-length. | Intensity. | Wave-length. | Intensity. |
|---|---|---|---|---|---|---|---|
| 4521·42 | 35·6 | 4579·99 | 286·0 | 4662·81 | 138·0 | 4743·38 | 44·0 |
| 21·49 | | 81·54 | 13·4 | 64·63 | 5·3 | 45·31 | 11·2 |
| 22·45 | 3·1 | 82·59 | 123·0 | 65·59 | 44·4 | 45·97 | 3·5 |
| 22·87 | 13·7 | 83·88 | 9·3 | 65·77 | 7·3 | 50·73 | 5·6 |
| 23·19 | 14·3 | 84·50 | 54·3 | 67·08 | 13·4 | 51·58 | 4·1 |
| 24·14 | 27·1 | 85·12 | 2·0 | 67·79 | 39·3 | 55·41 | 5·5 |
| 24·88 | 4·1 | 88·68 | 30·7 | 69·28 | 14·0 | 56·95 | 14·1 |
| 27·18 | 15·1 | 89·92 | 4·0 | 70·02 | 8·3 | 60·12 | 7·6 |
| 29·08 | 7·6 | 91·81 | 11·6 | 70·65 | 31·0 | 63·84 | 76·8 |
| 29·27 | 12·4 | 94·74 | 4·0 | 71·31 | 60·9 | 67·25 | 13·3 |
| 30·89 | 6·6 | 95·17 | 7·6 | 71·71 | 14·7 | 67·92 | 3·5 |
| 31·19 | 21·3 | 97·21 | 23·0 | 72·08 | 6·7 | 68·18 | 4·0 |
| 31·95 | 4·8 | 98·49 | 6·7 | 73·10 | 16·1 | 69·52 | 3·9 |
| 33·06 | 32·7 | 4600·86 | 7·3 | 73·23 | 11·4 | 70·61 | 18·9 |
| 33·09 | | 05·36 | 4·5 | 74·53 | 35·1 | 70·91 | 10·2 |
| 33·13 | | 07·09 | 6·9 | 74·96 | 29·7 | 74·27 | 13·0 |
| 34·16 | 48·4 | 07·40 | 18·2 | 75·31 | 34·3 | 75·86 | 8·7 |
| 34·63 | 61·0 | 08·56 | 1·7 | 78·15 | 2·7 | 77·45 | 43·0 |
| 35·91 | 11·4 | 13·12 | 24·0 | 79·09 | 38·8 | 80·92 | 51·9 |
| 37·73 | 3·2 | 14·59 | 17·4 | 80·43 | 39·3 | 80·96 | |
| 37·88 | 11·9 | 17·53 | 81·0 | 80·74 | 7·8 | 80·98 | |
| 38·31 | 7·3 | 18·13 | 17·6 | 81·35 | 10·6 | 82·44 | 8·0 |
| 39·16 | 8·2 | 18·30 | 35·8 | 82·34 | 71·5 | 82·87 | 5·5 |
| 41·12 | 9·0 | 18·60 | 15·2 | 83·82 | 159·0 | 84·78 | 10·4 |
| 42·95 | 4·6 | 20·76 | 19·1 | 84·65 | 27·5 | 85·09 | 6·7 |
| 43·69 | 23·8 | 24·10 | 7·6 | 86·14 | 29·0 | 85·98 | 10·9 |
| 47·23 | 2·4 | 24·73 | 4·8 | 86·77 | 88·0 | 89·42 | 39·5 |
| 47·97 | 27·1 | 25·31 | 39·2 | 88·44 | 15·4 | 90·86 | 17·0 |
| 49·90 | 22·7 | 25·58 | 13·5 | 90·18 | 50·6 | 91·22 | 8·2 |
| 50·98 | 28·2 | 26·76 | 4·1 | 92·04 | 25·1 | 93·91 | 49·5 |
| 51·72 | 17·6 | 27·99 | 227·0 | 93·81 | 2·8 | 94·19 | 12·4 |
| 52·42 | 9·5 | 28·71 | 6·6 | 99·83 | 5·7 | 95·15 | 11·4 |
| 54·16 | 107·0 | 29·67 | 6·0 | 4701·72 | 5·9 | 96·99 | 45·0 |
| 57·13 | 35·6 | 31·07 | 6·5 | 02·56 | 17·7 | 97·05 | |
| 57·39 | 32·0 | 31·46 | 160·0 | 05·26 | 8·2 | 97·10 | |
| 58·32 | 25·4 | 31·85 | 233·0 | 08·49 | 10·0 | 97·75 | 72·2 |
| 58·61 | 31·4 | 34·03 | 485·0 | 09·54 | 80·0 | 99·15 | 3·1 |
| 58·84 | 8·2 | 34·60 | 148·0 | 11·07 | 11·2 | 4801·99 | 12·2 |
| 60·21 | 13·1 | 34·62 | | 13·93 | 47·1 | 02·40 | 13·4 |
| 60·59 | 4·1 | 34·71 | | 14·31 | 7·3 | 04·07 | 5·3 |
| 61·15 | 20·9 | 38·47 | 6·4 | 19·04 | 185·0 | 07·34 | 5·9 |
| 62·22 | 52·5 | 43·25 | 4·0 | 19·30 | 12·5 | 07·49 | 4·4 |
| 62·45 | 8·3 | 43·85 | 5·3 | 20·50 | 3·7 | 13·60 | 31·0 |
| 63·73 | 19·0 | 45·34 | 10·2 | 21·00 | 4·4 | 17·51 | 17·8 |
| 64·91 | 4·7 | 46·58 | 2·8 | 21·54 | 19·8 | 19·22 | 7·8 |
| 65·54 | 21·1 | 49·27 | 6·7 | 23·03 | 127·0 | 22·94 | 52·1 |
| 68·13 | 188·0 | 49·50 | 13·6 | 23·84 | 5·3 | 24·57 | 6·5 |
| 68·62 | 6·7 | 50·38 | 9·9 | 24·82 | 27·6 | 30·63 | 9·2 |
| 70·80 | 5·6 | 50·95 | 11·6 | 26·14 | 8·3 | 30·78 | 8·0 |
| 72·23 | 18·6 | 51·51 | 5·0 | 27·74 | 6·0 | 31·56 | 8·5 |
| 72·71 | 134·0 | 53·00 | 87·0 | 28·50 | 3·4 | 32·79 | 10·4 |
| 75·88 | 73·0 | 53·20 | 19·4 | 28·89 | 2·9 | 38·24 | 34·5 |
| 76·54 | 7·4 | 54·06 | 20·1 | 30·75 | 5·9 | 41·52 | 5·0 |
| 76·73 | 6·6 | 57·86 | 10·5 | 32·73 | 13·4 | 41·72 | 6·2 |
| 77·32 | 3·2 | 58·78 | 8·5 | 38·71 | 4·2 | 42·39 | 10·8 |
| 78·02 | 76·0 | 60·10 | 7·9 | 40·99 | 37·1 | 43·24 | 35·8 |
| 78·56 | 6·2 | 60·40 | 57·0 | 42·11 | 18·8 | 43·43 | 7·3 |
| 79·45 | 60·0 | 61·40 | 126·0 | 42·78 | 58·6 | 43·76 | 8·7 |

Table II—continued.

| Wave-length. | Intensity. | Wave-length. | Intensity. | Wave-length. | Intensity. | Wave-length. | Intensity. |
|---|---|---|---|---|---|---|---|
| 4845·50 | 10·0 | 4936·14 | 11·5 | 5020·74 | 20·3 | 5153·87 | 20·5 |
| 48·11 | 5·9 | 36·43 | 11·2 | 24·96 | 3·3 | 56·26 | 8·8 |
| 49·30 | 73·7 | 36·71 | 8·0 | 27·70 | 4·1 | 56·84 | 10·7 |
| 49·53 | 7·9 | 37·32 | 5·5 | 28·85 | 10·5 | 58·84 | 4·0 |
| 49·85 | 9·8 | 39·16 | 18·5 | 30·37 | 41·5 | 59·83 | 7·7 |
| 56·55 | 60·5 | 39·60 | 29·0 | 32·15 | 4·5 | 60·53 | 9·2 |
| 60·11 | 22·0 | 40·01 | 6·4 | 34·26 | 3·0 | 67·41 | 5·9 |
| 66·31 | 12·0 | 41·99 | 4·3 | 39·82 | 52·0 | 68·24 | 20·5 |
| 67·03 | 16·7 | 42·55 | 10·7 | 41·63 | 36·0 | 70·17 | 6·1 |
| 69·45 | 21·9 | 43·61 | 3·3 | 43·92 | 6·8 | 73·78 | 9·0 |
| 70·29 | 4·5 | 44·82 | 14·7 | 47·72 | 4·2 | 74·70 | 14·5 |
| 73·01 | 95·0 | 45·80 | 4·0 | 48·00 | 16·2 | 78·49 | 5·0 |
| 73·32 | 20·0 | 49·54 | 5·5 | 49·37 | 9·9 | 80·58 | 16·5 |
| 74·29 | 29·5 | 52·59 | 8·3 | 50·42 | 4·4 | 88·29 | 7·5 |
| 75·96 | 34·0 | 55·00 | 3·4 | 55·09 | 67·0 | 90·39 | 8·1 |
| 78·13 | 14·4 | 55·49 | 3·5 | 61·73 | 27·0 | 91·03 | 9·3 |
| 81·52 | 12·1 | 55·76 | 17·5 | 63·88 | 33·0 | 93·01 | 7·5 |
| 82·78 | 7·0 | 56·79 | 24·5 | 67·48 | 26·0 | 96·38 | 29·0 |
| 83·86 | 9·0 | 60·12 | 3·7 | 68·12 | 48·0 | 97·21 | 20·0 |
| 86·41 | 5·0 | 60·95 | 15·0 | 69·66 | 8·1 | 97·52 | 6·9 |
| 86·90 | 7·6 | 65·09 | 8·9 | 70·30 | 9·0 | 99·71 | 12·7† |
| 88·48 | 11·1 | 66·91 | 35·0* | 72·31 | 9·9 | 5202·03 | 6·6 |
| 91·27 | 9·6 | 67·86 | 6·5 | 72·62 | 10·3 | 03·02 | 9·8 |
| 91·94 | 5·4 | 68·63 | 4·1 | 75·44 | 23·3 | 04·33 | 5·8 |
| 96·47 | 6·8 | 69·22 | 26·0 | 76·14 | 10·2 | 08·44 | 2·8 |
| 96·89 | 3·8 | 70·71 | 6·6 | 77·20 | 7·8 | 11·51 | 3·4 |
| 97·48 | 2·5 | 71·76 | 8·0 | 78·78 | 4·6 | 14·62 | 16·5 |
| 4900·89 | 14·0 | 73·31 | 56·0 | 80·49 | 44·5 | 15·60 | 5·5 |
| 01·87 | 12·0 | 76·63 | 18·4 | 80·96 | 16·6 | 21·13 | 6·4 |
| 03·59 | 2·8 | 77·17 | 6·1 | 81·43 | 14·2 | 21·45 | 8·3 |
| 06·02 | 6·5 | 78·26 | 16·3 | 81·93 | 29·5 | 22·85 | 15·5 |
| 06·34 | 6·0 | 79·12 | 9·5 | 82·77 | 12·0 | 23·54 | 8·5 |
| 06·78 | 4·3 | 80·48 | 24·5 | 84·84 | 46·0 | 24·40 | 3·7 |
| 08·06 | 12·0 | 81·16 | 4·7 | 90·22 | 8·9 | 24·83 | 4·0 |
| 08·78 | 13·5 | 83·18 | 11·0 | 92·28 | 4·3 | 26·77 | 27·0 |
| 12·32 | 3·7 | 83·52 | 4·7 | 94·71 | 3·2 | 30·49 | 5·0 |
| 15·00 | 3·1 | 90·15 | 17·0 | 96·21 | 4·4 | 31·71 | 7·1 |
| 16·27 | 1·8 | 94·09 | 7·7 | 99·75 | 12·0 | 39·01 | 18·6 |
| 19·13 | 11·4 | 95·21 | 3·3 | 5103·57 | 25·0 | 39·82 | 4·1 |
| 20·33 | 6·3 | 96·46 | 7·8 | 06·79 | 6·8 | 41·29 | 6·3 |
| 21·20 | 7·6 | 96·85 | 10·8 | 07·64 | 17·0 | 43·72 | 5·2 |
| 22·45 | 8·0 | 97·94 | 11·7 | 08·36 | 3·8 | 44·64 | 7·5 |
| 24·02 | 8·0 | 5000·22 | 7·0 | 09·31 | 14·3 | 52·56 | 3·2 |
| 25·23 | 12·0 | 03·40 | 40·0 | 11·74 | 4·9 | 56·61 | 24·0 |
| 25·78 | 2·7 | 07·99 | 28·0 | 13·13 | 51·0 | 59·38 | 7·5 |
| 26·26 | 7·1 | 08·40 | 8·5 | 15·35 | 10·6 | 59·91 | 4·5 |
| 28·37 | 22·5 | 08·54 | 8·4 | 16·94 | 4·8 | 61·18 | 16·5 |
| 28·64 | 88·0 | 08·62 |  | 17·39 | 8·0 | 63·90 | 11·7 |
| 28·80 |  | 08·66 |  | 20·98 | 9·4 | 64·28 | 5·3 |
| 32·26 | 34·0 | 09·62 | 9·2 | 22·58 | 17·6 | 64·68 | 11·1 |
| 33·52 | 30·0 | 11·19 | 52·0 | 32·03 | 9·4 | 66·05 | 34·0 |
| 33·84 | 10·0 | 13·04 | 92·0 | 34·12 | 5·2 | 68·24 | 10·0 |
| 34·24 | 110·0 | 14·47 | 26·0 | 37·11 | 8·2 | 70·41 | 16·0 |
| 34·58 | 5·0 | 15·07 | 55·0 | 43·42 | 6·5 | 72·30 | 27·0 |
| 35·24 | 19·0 | 16·50 | 33·0 | 43·57 | 2·0 | 78·33 | 12·5 |
| 35·94 | 9·9 | 17·13 | 16·2 | 46·34 | 32·5 | 80·51 | 4·5 |

* Possibly a little blended by 4966·70.

† Double ?

Table II—continued.

| Wave-length. | Intensity. | Wave-length. | Intensity. | Wave-length. | Intensity. | Wave-length. | Intensity. |
|---|---|---|---|---|---|---|---|
| 5283·29 | 9·3 | 5387·53 | 10·9 | 5462·99 | 14·5 | 5555·10 | 9·1 |
| 84·50 | 13·7 | 88·17 | 43·0 | 65·19 | 2·9 | 56·48 | 3·1 |
| 90·37 | 4·2 | 90·52 | 5·3 | 66·46 | 11·4 | 57·38 | 1·8 |
| 90·56 | 3·3 | 91·14 | 9·3 | 70·10 | 2·6 | 57·95 | 2·7 |
| 91·60 | 26·5 | 91·54 | 9·0 | 70·53 | 3·0 | 58·92 | 2·9 |
| 96·09 | 5·7 | 92·29 | 52·0 | 71·58 | 3·4 | 61·74 | 11·8 |
| 99·70 | 6·7 | 93·53 | 2·7 | 71·84 | 2·8 | 62·24 | 6·8 |
| 5302·11 | 9·0 | 94·07 | 3·2 | 73·30 | 5·1 | 64·51 | 17·3 |
| 03·10 | 43·6 | 94·39 | 13·4 | 74·86 | 30·0 | 66·19 | 2·6 |
| 04·42 | 20·1 | 94·80 | 3·6 | 76·27 | 8·3 | 69·50 | 2·5 |
| 05·57 | 2·3 | 98·07 | 21·4 | 77·18 | 3·0 | 71·59 | 3·6 |
| 08·61 | 4·5 | 98·97 | 19·2 | 77·82 | 2·0 | 73·52 | 1·9 |
| 09·04 | 10·9 | 5400·07 | 3·9 | 79·90 | 3·2 | 73·92 | 8·6 |
| 13·59 | 5·3 | 01·05 | 15·7 | 81·08 | 32·7 | 78·71 | 6·0 |
| 14·35 | 6·2 | 01·72 | 5·6 | 82·85 | 3·2 | 79·47 | 2·5 |
| 15·17 | 6·3 | 03·20 | 4·8 | 83·55 | 2·6 | 79·59 | 6·3 |
| 17·89 | 16·0 | 03·93 | 3·4 | 85·72 | 2·4 | 79·96 | 4·1 |
| 19·16 | 22·1 | 05·33 | 16·0 | 88·29 | 2·8 | 83·04 | 6·7 |
| 20·43 | 7·8 | 05·74 | 4·9 | 90·16 | 2·8 | 83·34 | 2·1 |
| 21·50 | 2·0 | 08·79 | 16·7 | 91·25 | 3·2 | 85·93 | 2·6 |
| 26·78 | 9·2 | 09·69 | 21·0 | 92·97 | 10·8 | 90·09 | 3·5 |
| 31·61 | 6·0 | 10·22 | 7·5 | 95·96 | 24·9 | 91·42 | 2·4 |
| 32·15 | 3·4 | 17·80 | 45·6 | 96·63 | 5·6 | 97·64 | 30·0 |
| 33·23 | 3·5 | 19·89 | 60·9 | 97·71 | 3·2 | 99·51 | 2·7 |
| 34·26 | 21·1 | 21·14 | 8·1 | 99·58 | 45·8 | 5600·42 | 23·6 |
| 36·32 | 12·5 | 21·32 | 7·2 | 5500·48 | 10·0 | 01·70 | 5·8 |
| 36·58 | 26·0 | 22·13 | 14·6 | 05·52 | 32·7 | 04·05 | 2·3 |
| 39·39 | 5·4 | 23·25 | 11·5 | 06·34 | 18·4 | 04·36 | 2·7 |
| 40·82 | 4·9 | 25·20 | 22·0 | 07·85 | 7·3 | 04·69 | 14·1 |
| 43·17 | 3·3 | 25·89 | 38·8 | 08·09 | 3·0 | 12·54 | 57·8 |
| 44·79 | 24·6 | 26·32 | 18·6 | 10·26 | 2·5 | 16·23 | 5·1 |
| 45·85 | 3·1 | 26·47 | 10·0 | 13·92 | 2·9 | 18·29 | 2·9 |
| 50·71 | 4·7 | 28·38 | 4·2 | 14·60 | 7·9 | 20·91 | 11·3 |
| 51·74 | 5·1 | 28·95 | 11·9 | 17·48 | 2·8 | 23·08 | 14·2 |
| 52·29 | 1·7 | 29·31 | 4·3 | 18·47 | 25·1 | 24·31 | 7·8 |
| 54·75 | 8·0 | 30·15 | 3·5 | 20·88 | 11·5 | 25·91 | 2·9 |
| 55·91 | 40·2 | 30·87 | 12·4 | 23·97 | 7·9 | 26·72 | 2·5 |
| 58·24 | 1·9 | 32·32 | 2·9 | 24·15 | 8·2 | 27·44 | 5·0 |
| 58·73 | 10·8 | 34·82 | 30·0 | 26·32 | 8·3 | 30·62 | 12·8 |
| 61·59 | 2·4 | 36·33 | 2·3 | 27·35 | 6·1 | 30·99 | 8·5 |
| 62·38 | 2·4 | 38·78 | 10·6 | 27·79 | 2·2 | 32·19 | 7·5 |
| 62·84 | 15·9 | 39·69 | 5·8 | 29·51 | 4·2 | 34·16 | 9·7 |
| 63·51 | 8·4 | 40·19 | 3·3 | 29·87 | 2·8 | 34·81 | 31·8 |
| 65·90 | 14·1 | 42·21 | 3·5 | 34·05 | 5·2 | 40·42 | 2·9 |
| 68·36 | 3·9 | 42·52 | 2·1 | 34·48 | 2·0 | 42·07 | 2·3 |
| 71·90 | 9·0 | 44·35 | 2·3 | 35·98 | 26·2 | 42·72 | 5·9 |
| 72·45 | 8·8 | 46·67 | 4·0 | 36·35 | 3·7 | 42·94 | 15·4 |
| 73·08 | 9·0 | 49·85 | 2·7 | 37·47 | 73·5 | 46·11 | 8·8 |
| 73·41 | 16·3 | 52·53 | 2·7 | 39·96 | 2·6 | 52·18 | 6·0 |
| 74·29 | 5·1 | 54·74 | 3·5 | 43·11 | 20·0 | 54·76 | 9·7 |
| 75·62 | 2·1 | 55·32 | 11·5 | 43·50 | 20·0 | 55·75 | 26·5 |
| 76·51 | 1·9 | 56·69 | 5·2 | 44·68 | 2·6 | 57·80 | 3·3 |
| 77·20 | 3·1 | 56·98 | 9·9 | 46·49 | 2·9 | 60·79 | 2·8 |
| 78·39 | 6·7 | 57·91 | 2·7 | 47·63 | 12·1 | 61·63 | 14·8 |
| 79·52 | 4·9 | 58·79 | 5·6 | 48·40 | 3·7 | 61·84 | 7·7 |
| 79·98 | 8·8 | 59·60 | 43·0 | 49·47 | 4·5 | 62·87 | 9·2 |
| 85·51 | 42·0 | 61·40 | 3·8 | 49·74 | 8·2 | 70·28 | 3·0 |
| 86·20 | 10·6 | 61·84 | 8·3 | 52·53 | 26·3 | 70·76 | 9·5 |
| 86·75 | 13·4 | 62·30 | 3·2 | 53·83 | 4·9 | 70·93 | 13·0 |

Table II—continued.

| Wave-length. | Intensity. | Wave-length. | Intensity | Wave-length. | Intensity. | Wave-length. | Intensity. |
|---|---|---|---|---|---|---|---|
| 5672·37 | 2·8 | 5801·15 | 10·8 | 5947·30 | 38·0 | 6135·40 | 78·0 |
| 74·98 | 10·5 | 06·10 | 23·0 | 47·99 | 10·0 | 39·37 | 8·6 |
| 79·02 | 2·3 | 11·50 | 14·3 | 49·90 | 52·0 | 46·19 | 17·9 |
| 82·51 | 3·1 | 12·59 | 44·0 | 59·81 | 34·7 | 46·90 | 11·3 |
| 83·08 | 7·1 | 14·94 | 22·9 | 63·47 | 12·0 | 51·47 | 12·0 |
| 83·74 | 19·4 | 16·44 | 13·7 | 67·27 | 15·0 | 55·63 | 28·0 |
| 84·13 | 22·0 | 17·08 | 8·9 | 70·31 | 16·7 | 59·58 | 19·6 |
| 84·54 | 5·7 | 17·60 | 10·7 | 70·93 | 15·3 | 61·61 | 36·0 |
| 87·46 | 3·1 | 19·28 | 9·1 | 74·14 | 11·0 | 62·50 | 10·0 |
| 87·92 | 3·4 | 22·07 | 13·9 | 75·44 | 120·0 | 67·74 | 21·7 |
| 89·20 | 34·6 | 22·76 | 37·8 | 82·56 | 21·8 | 69·64 | 27·4 |
| 91·16 | 13·3 | 24·56 | 9·3 | 89·24 | 14·0 | 74·09 | 15·8 |
| 92·10 | 3·0 | 31·02 | 10·2 | 90·53 | 19·0 | 76·23 | 15·5 |
| 94·14 | 25·0 | 32·77 | 17·6 | 94·06 | 40·0 | 82·99 | 69·3 |
| 96·18 | 9·9 | 36·13 | 45·2 | 6002·82 | 18·1 | 97·11 | 18·4 |
| 96·87 | 3·2 | 49·32 | 17·0 | 07·18 | 8·6 | 97·74 | 12·9 |
| 97·40 | 6·0 | 50·89 | 9·2 | 11·40 | 8·4 | 99·39 | 69·0 |
| 97·53 | 11·4 | 51·62 | 9·8 | 18·29 | 173·0 | 6201·18 | 37·5 |
| 5700·64 | 9·6 | 59·81 | 20·5 | 21·27 | 27·0 | 24·81 | 137·0 |
| 03·25 | 12·0 | 61·18 | 9·3 | 23·75 | 47·0 | 30·26 | 44·5 |
| 03·76 | 11·1 | 64·46 | 15·0 | 25·77 | 8·0 | 33·01 | 20·6 |
| 09·77 | 12·1 | 69·26 | 20·2 | 27·98 | 34·7 | 35·89 | 11·7 |
| 13·45 | 33·5 | 71·95 | 25·6 | 30·05 | 10·8 | 38·39 | 68·0 |
| 16·01 | 9·6 | 78·50 | 30·9 | 31·47 | 24·5 | 49·16 | 15·8 |
| 23·45 | 10·0 | 79·20 | 14·9 | 31·90 | 81·1 | 62·51 | 16·4 |
| 27·05 | 12·4 | 82·00 | 11·0 | 41·03 | 11·1 | 70·54 | 15·0 |
| 28·55 | 30·7 | 83·94 | 21·3 | 42·71 | 18·5 | 71·31 | 26·3 |
| 31·93 | 19·6 | 84·63 | 22·7 | 44·65 | 7·4 | 74·84 | 19·8 |
| 35·13 | 17·1 | 87·35 | 11·0 | 45·42 | 8·7 | 85·39 | 46·3 |
| 36·88 | 40·3 | 88·17 | 28·0 | 47·85 | 14·2 | 99·42 | 64·3 |
| 38·42 | 12·0 | 89·03 | 17·5 | 52·37 | 16·8 | 6303·49 | 21·4 |
| 57·35 | 11·7 | 5901·21 | 7·7 | 53·27 | 15·0 | 20·38 | 13·9 |
| 59·56 | 15·6 | 03·50 | 9·8 | 56·10 | 21·3 | 27·06 | 91·0 |
| 60·39 | 16·2 | 09·40 | 10·9 | 62·62 | 11·9 | 29·81 | 25·2 |
| 62·72 | 9·4 | 10·17 | 13·0 | 63·29 | 30·6 | 32·49 | 32·1 |
| 65·89 | 8·8 | 16·06 | 16·3 | 66·63 | 24·4 | 40·57 | 44·2 |
| 66·28 | 11·5 | 16·51 | 10·9 | 67·72 | 32·3 | 62·48 | 32·5 |
| 66·99 | 8·9 | 18·08 | 15·0 | 69·99 | 22·6 | 64·62 | 9·6 |
| 73·22 | 15·6 | 20·49 | 22·3 | 74·39 | 20·8 | 70·13 | 10·2 |
| 74·58 | 16·2 | 24·83 | 39·4 | 78·90 | 14·6 | 72·21 | 15·8 |
| 75·05 | 37·0 | 25·80 | 10·5 | 80·78 | 97·0 | 76·08 | 9·5 |
| 78·98 | 14·6 | 31·37 | 37·5 | 90·91 | 26·1 | 79·21 | 13·3 |
| 80·05 | 12·0 | 32·02 | 10·8 | 95·96 | 67·0 | 80·11 | 12·0 |
| 83·00 | 9·3 | 32·30 | 10·2 | 98·22 | 44·1 | 82·90 | 8·9 |
| 85·21 | 17·5 | 36·03 | 10·3 | 6107·83 | 8·4 | 97·44 | 8·2 |
| 85·77 | 46·4 | 37·99 | 10·1 | 12·79 | 9·0 | 99·28 | 48·5 |
| 88·26 | 13·9 | 38·62 | 37·7 | 16·72 | 9·7 | 6428·11 | 29·6 |
| 89·85 | 9·4 | 41·14 | 7·9 | 21·79 | 152·0 | 29·31 | 16·1 |
| 91·69 | 17·1 | 41·98 | 8·7 | 27·24 | 51·0 | 33·49 | 12·8 |
| 94·61 | 11·0 | 42·95 | 6·7 | 27·64 | 29·5 | 34·84 | 16·2 |
| 98·96 | 9·9 | 43·55 | 10·4 | 34·31 | 22·3 | 41·50 | 18·0 |

It is a pleasure to us to express our gratitude to Prof. Ornstein for his great interest in this work.

One of us, W. Kapuscinski, takes this occasion also to thank the International Education Board, which enabled him to co-operate in this work.

# *The Form of the Central Carbon Atom in Pentaerythritol Tetra-acetate as shown by X-ray Crystal Analysis.*

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[*Plates* 3, 4.]

(*Communicated by Sir William Bragg, F.R.S.—Received August 21, 1928.*)

## *Introduction.*

A survey of those organic compounds in which carbon prevails seems to indicate that the carbon atom has a tendency to preserve the tetrahedral symmetry which it exhibits in diamond. It is to be expected, however, that this symmetry may be distorted to some extent, when the carbon atom is associated with other atoms or groups of atoms. In the present paper an attempt is made to study the behaviour of the central carbon atom in pentaerythritol tetra-acetate, $C(CH_2OCOCH_3)_4$, where the carbon atom is associated with four like radicals of relatively large molecular weight.

## *Crystallographic Data.*

Pentaerythritol tetra-acetate crystallises from dilute alcohol in tetragonal prismatic needles, which are occasionally terminated by a tetragonal pyramid. The crystals were previously described* as tetragonal with an axial ratio $a : c = 1 : 0 \cdot 324$ and the class uncertain. The density $D_{4°}^{18°}$ was found to be 1·273 (through an undetected printer's error it was given as 1·213) and the refractive indices $\Sigma = 1 \cdot 483$ and $\omega = 1 \cdot 433$.

## *Results of X-ray Analysis.*

The crystals were examined in the usual way by taking rotation, oscillation and Laue photographs (Plates 3, 4). The X-ray source was a Shearer tube with copper anticathode ($\lambda k_\alpha = 1 \cdot 539$ Å.U.).

The axes of the unit cell were found to be

$$a = 11 \cdot 98 \text{ Å.U.}$$
$$c = 5 \cdot 47 \text{ Å.U.}$$

with an error of approximately 0·2 per cent.

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* Knaggs, 'J. Chem. Soc. Lond. Trans.,' vol. 123, p. 77 (1923).

N, the number of molecules per unit cell is given by $11 \cdot 98^2 \times 5 \cdot 47 \times \rho = \mathrm{N} \times \mathrm{M} \times 1 \cdot 65$. The density $\rho$ being 1·273, and M, the molecular weight referred to oxygen as 16, is equal to 304. Therefore

$$\mathrm{N} = \frac{11 \cdot 98^2 \times 5 \cdot 47 \times 1 \cdot 273}{304 \times 1 \cdot 65} = 1 \cdot 99,$$

*i.e.*, there are two molecules in the unit cell.

The axial ratio obtained from X-ray measurements is $a : c = 1 : 0 \cdot 457$. An almost identical value $1 : 0 \cdot 324 \times \sqrt{2} = 1 : 0 \cdot 458$ results from crystallographic measurements, provided that the axes are referred to the smallest unit cell obtained from X-ray observations.

It was soon seen that the crystals had not the symmetry of the ditetragonal bipyramidal (or holohedral) class, but only that of the tetragonal bipyramidal class, there being no planes of symmetry parallel to the tetragonal axis. This is well shown in a series of oscillation photographs about the $c$-axis, of which the one due to oscillation through five degrees on either side of the (110) plane is reproduced here. The Laue photograph (also reproduced in this paper) taken with the $c$-axis vertical and the X-ray beam perpendicular to the (100) plane shows only one plane of symmetry, and that perpendicular to the $c$-axis.

In order to find the space-group, a number of reflections from planes having spacings ranging from those of the axial planes down to about 1·7 Å.U. have been identified. This was done with the aid of Bernal's method,* which was found to be extremely useful in this case. No general halvings were found, but it was noticed that no odd order reflections from planes of the form $(hko)$, where $(h+k)$ is odd, appeared on the photographs. This led to the conclusion that the crystals are built on a simple tetragonal lattice, $\Gamma_t$, the only possible space-groups being $C_{4h}^3$ and $C_{4h}^4$. In addition to the halvings mentioned above, it was found that the (001) plane was also halved, from which it is concluded that the space-group is $C_{4h}^4$.

Since the (001) halving is of very great importance in determining the molecular symmetry, the observations, which led to it will be described in detail. The rotation photographs about the [100] and [110] axes show a reflection for the second order only of the (001) plane. In the [100] photograph, a spot is found on the zero layer line in such a position that it might be due to the $k_\alpha$ reflection from the (001) plane or to the $k_\beta$ reflection from the (011) plane. Now, for the distance, 3 cm., from crystal to photographic plate as used in these photographs, the calculated positions of the two reflections differ only by 0·06 mm., so that by their position alone they are indistinguishable. But in the [110] axis photograph, the spot no longer appears. It must, therefore, be due to the (011) $k_\beta$ reflection, for if it were due to the (001) $k_\alpha$ reflection, it should still appear in the same position as before. As a further test, a careful examination on the Bragg ionisation spectrometer was made for the various orders of the (001) plane, both by Mrs. Kathleen Lonsdale (to whom the author's thanks are due) and by the author, with the result that all orders except the second up to the eighth order were found to be absent.

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* Bernal, 'Roy. Soc. Proc.,' A, vol. 113, p. 117 (1926).

As an alternative, it might be suggested that the crystals belong to the tetragonal pyramidal class without a plane of symmetry perpendicular to the tetragonal axis. Whether this plane of symmetry really exists or not, it would appear in an X-ray examination, because owing to their automatic addition of a centre of symmetry, the X-rays cannot distinguish between an axis of symmetry with a symmetry plane perpendicular to it and an axis of symmetry alone. But the halvings of the spacings of the (*hko*) planes, where $(h+k)$ is odd, makes the tetragonal pyramidal class unlikely. For, if the crystals belong to that class, these halvings must be regarded as accidental.* It may be emphasised too that by means of a series of oscillation photographs about the [001] axis, the crystals have been specially explored for (*hko*) planes.

The space-group $C_{4h}{}^1$ with only two molecules per unit cell necessitates each molecule having four-fold symmetry, the only possible type in this space-group being a four-fold alternating axis. The molecule is of the form shown in fig. 1. The four $-CH_2OCOCH_3$ radicals attached to the central carbon atom must be regarded as four asymmetric units and the symmetry of the central carbon atom must approximate to that required by the space-group, *i.e.*, a four-fold alternating axis. Such an arrangement is well in accord with chemical and physical considerations, the valency distribution from the central carbon atom being a reasonable one.

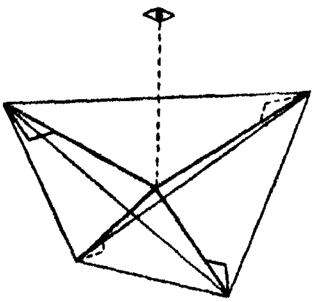

FIG. 1.

A. Gerstäcker, H. Möller and A. Reis† recently published an account of an X-ray examination of pentaerythritol tetra-acetate, in which they describe the crystals as belonging to the space-group $C_{4h}{}^3$, and arrive at the conclusion that the molecule has a simple tetragonal axis of symmetry and is of the form shown in fig. 2 (reproduced from fig. 1 of the author's paper). Here all four valency bonds from the central carbon atom are directed away from it towards a square base, giving polarity to the molecule. Such a distribution of the valencies of a carbon atom is quite unsupported by any physical or chemical evidence. It is natural, therefore, to look for very weighty reasons before accepting such a view.

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* Astbury and Yardley, "Tabulated Data for the Examination of the 230 Space-groups by Homogeneous X-rays," 'Phil. Trans. Roy. Soc., Lond.,' A, vol. 224, p. 239 (1924).

† 'Z. Kryst.,' vol. 66, 3/4, p. 355 (1928).

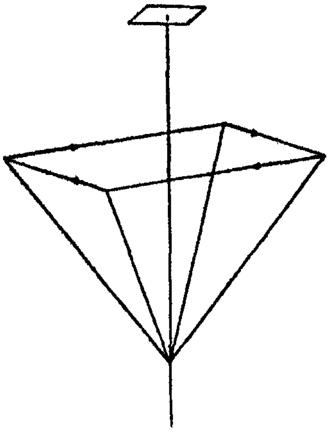

FIG. 2.

As pointed out elsewhere* the evidence shown by these authors for the space-group $C_{4h}^3$ is very slight, depending only on the observation of a reflection of the first order from the (001) plane. This reflection is only mentioned as occurring in an oscillation photograph about the [100] axis, using copper radiation, and neither the range of the oscillation nor its angular relation to any plane appears to be stated. It is not possible, from the information given, to say with certainty that this observed reflection is due to the $k_\alpha$ reflection from the (001) plane or that it is not due to the $k_\beta$ reflection from the $(0\bar{1}1)$ plane, as found here (see above).

Even if the space-group $C_{4h}^3$ given by Gerstäcker, Möller and Reis were correct, there would still be the choice between a tetragonal alternating axis of symmetry, where the central carbon atom of the molecule would be playing its expected part, and a simple tetragonal axis, where it would not. The authors have chosen the latter symmetry on the grounds that such a molecule would lead to a more chain-like structure than the former, and that on account of the prismatic growth of the crystals and the shortness of the *c*-axis compared with the *a*-axis, they would expect a chain structure. They also state that in a chain structure it is to be expected that the length of the chain will be parallel to the axis of highest symmetry of the crystal.

Now the results of X-ray crystal analysis, so far obtained, do not indicate an association between chain structure and prismatic growth. On the contrary, there is a strong tendency for crystals with a chain structure to adopt a thin tabular habit. Such is the case in the many long chain carbon compounds, which have been examined by X-rays and moreover in these the length of the chain is perpendicular to the plates. Again, prismatic growth is a common

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* Knaggs, 'Nature,' vol. 121, p. 616 (1928).

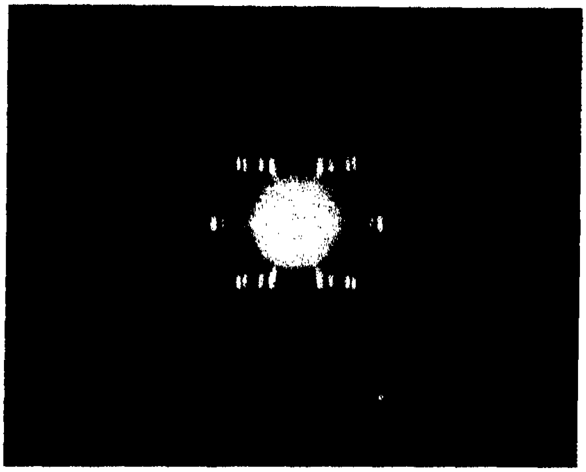

Fig. 1.—Rotation about *c* Axis.

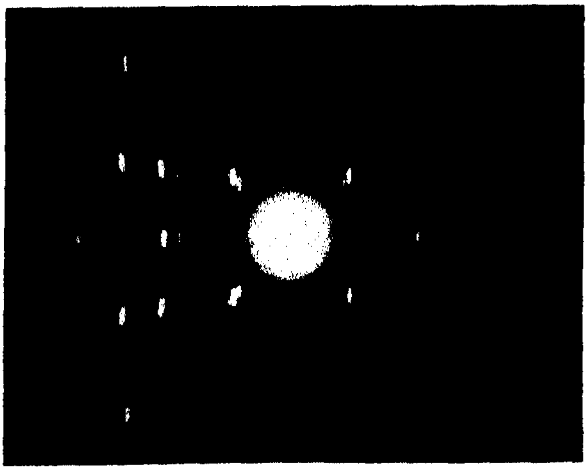

Fig. 2.—Oscillation about *c* Axis, —5°...5° from 110.

(*Facing p.* 72.)

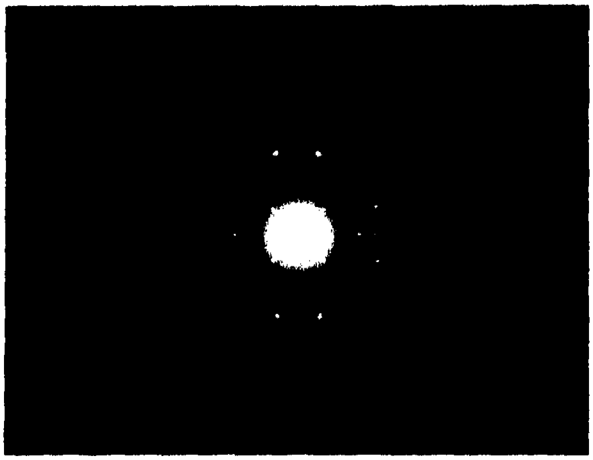

Fig. 3.—Rotation about *a* Axis.

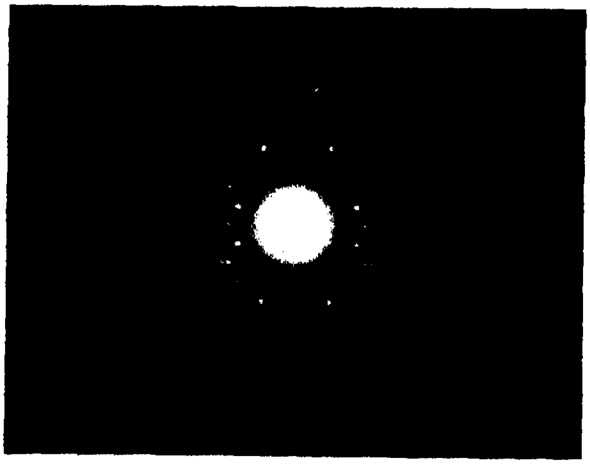

Fig. 4.—Rotation about [110] Axis.

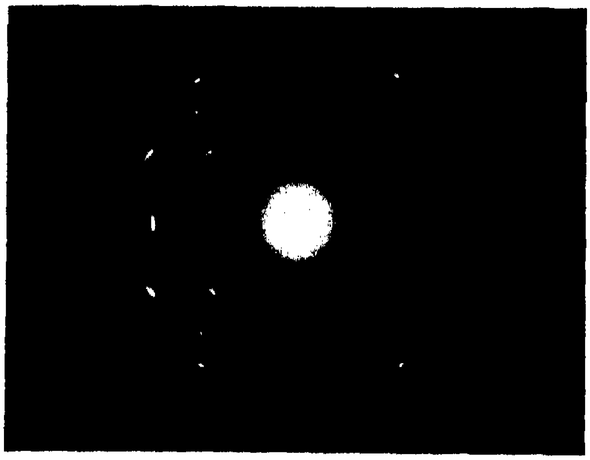

Fig. 5.—Laue photograph, perpendicular to (100).

feature of many crystals in which there is no approach to a chain structure, a striking example being the metallic tetraphenyl compounds examined by George.* So that even with the space-group $C_{4h}^3$ no valid reason has been given for regarding the molecule as having a simple tetragonal axis of symmetry with the consequent abnormal central carbon atom.

In the space-group $C_{4h}^4$ arrived at here, the two molecules of the unit cell have the equivalent positions 000 ; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Thus, there is a molecule situated at each corner of the unit cell, and at the centre of the cell a molecule, derived from any of the others by rotation about a screw axis, parallel to the *c*-axis and situated half way along an *a* or *b* edge of the cell or by reflection across a glide plane perpendicular to the *c*-axis.

Any attempt to discover the arrangement of the atoms in the cell will be made easier by the certain knowledge of the co-ordinates of the central carbon atoms of the two molecules, these being fixed by the molecular symmetry as 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The eight $-CH_2OCOCH_3$ groups must occupy the equivalent positions, $x\,y\,z$ ; $\bar{y}, x, z+\frac{1}{2}$ ; $\bar{x}\,\bar{y}\,z$ ; $y, \bar{x}, z+\frac{1}{2}$ ; $\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$ ; $y+\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z$ ; $x+\frac{1}{2}, y+\frac{1}{2}, \bar{z}$ ; $\frac{1}{2}-y, x+\frac{1}{2}, \frac{1}{2}-z$.† This results in there being 30 unknown parameters, since there are 10 atoms in each $-CH_2OCOCH_3$ group, and 3 parameters $x$, $y$, $z$ must be determined to fix the position of each atom. The labour involved in determining these parameters would be very great, and, in the present paper, it is not proposed to undertake any such complete solution. But a consideration of the relative intensities of some of the more important planes leads to certain suggestions as to what is likely to be the main outline of the structure.

In Table I is given the relative intensities observed for the strong planes and some of the weak planes of low indices. These intensities have been estimated by eye from overlapping oscillation photographs, and are only approximate and uncorrected for falling off of intensity with the reflecting angle. The standard used is that described by Robertson,‡ where very strong (v.s.), strong (s.), medium strong (m.s.), medium (m.), weak medium (w.m.), weak (w.), very weak (v.w.) are approximately in the ratio of 100 : 42 : 18 : 7 : 3 : 1·3 : 0·5.

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* George, 'Roy. Soc. Proc.,' A, vol. 113, p. 586 (1927).

† Wyckoff, 'The Analytical Expression of the Theory of Space-groups.'

‡ 'Roy. Soc. Proc.,' A, vol. 118, p. 712 (1928).

Table I.

| Intensity. | Planes. |
|---|---|
| v.s. | 101, 110. |
| s. | 201, 130, 111, 121, 241. |
| m.s. | 400, 310, 330, 240, 302, 211. |
| m. | 401, 420, 440, 131. |
| w.m. | 202, 222. |
| w. | 002, 600, 501, 601, 221. |
| v.w. or absent | 202, 402, 301, 220, 112, 311. |

Of the (*hko*) planes, it will be seen that the strongest reflections are obtained from the (110) and the (130) planes. It is likely, therefore, that the atoms of the $-CH_2OCOCH_3$ groups will be concentrated approximately in one of these two sets of planes. An arrangement in the 110 planes leads to a very uneven distribution of the atoms in the cell and one which is unlikely to be stable. But if the groups are arranged in the (130) planes, a very reasonable distribution results.

Of the (*hol*) planes, the (101) and the (201) give the strongest reflections, so that the $-CH_2OCOCH_3$ groups probably lie in or near one of these sets of planes. If in the (101) planes, then the (111) planes should give strong reflections, which they do. Arrangement in the (101) and (201) result in angles of about 132° and 95° respectively between the general directions of the $-CH_2OCOCH_3$ groups. It is still perfectly possible for the valency bonds from the central carbon atom to be directed tetrahedrally to the first carbon atoms of these groups, thus making an angle of 109° 28′ with one another, for the atoms of the groups will not be arranged in a straight line. On the other hand it is conceivable that there may be some distortion from the true tetrahedral angle, but this is not likely to be very great.

Figs. 3, 4 and 5 are drawn on the assumption that the $-CH_2OCOCH_3$ groups lie in or near the (130) and (101) planes. Fig. 3 shows the form the pentaerythritol molecule would then take. Fig. 4 is a projection on the (001) plane, the molecule in the centre being situated half-way down the cell with respect to those at the corners, part only of the latter being shown. Both these figures are simplified by the omission of hydrogen atoms. Fig. 5 is intended to represent the arrangement of the molecules as seen from the (100) plane. The broken lines represent molecules situated half-way between the (100) planes.

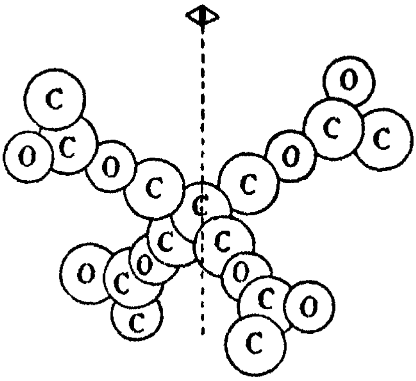

FIG. 3.

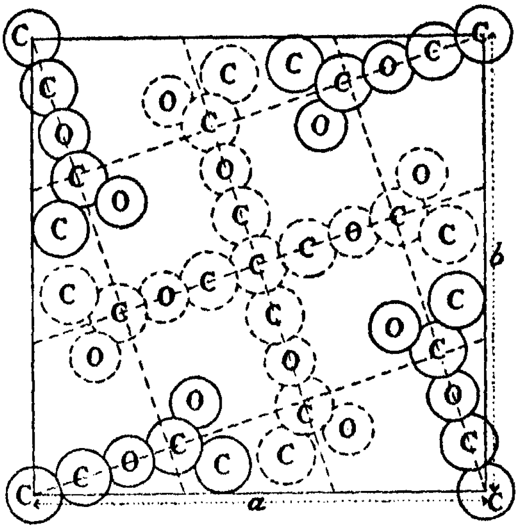

FIG. 4.

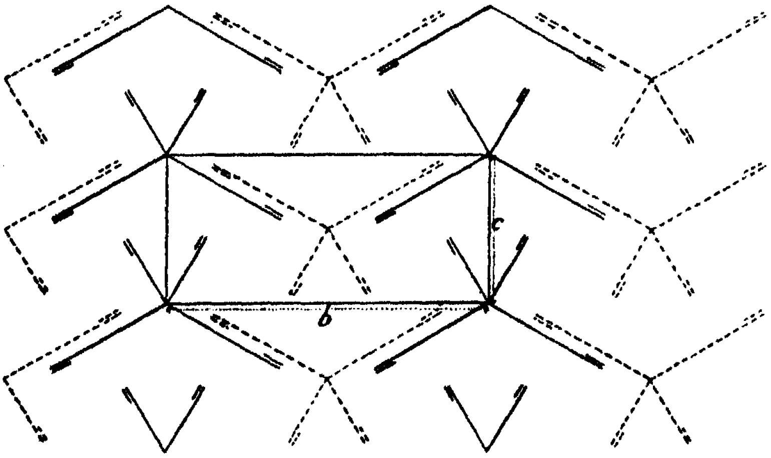

FIG. 5.

## *Summary.*

Pentaerythritol tetra-acetate is found to crystallise in the tetragonal bipyramidal class; the crystals are built on the Bravais lattice $\Gamma_t$ and the space-group $C_{4h}^4$; there are two molecules in the unit cell, which has the dimensions $11 \cdot 98^2 \times 5 \cdot 47$ A.U.

The molecules possess a four-fold alternating axis of symmetry.

A probable structure is suggested from which it follows that the symmetry of the central carbon atom may be tetrahedral, though some slight departure from true tetrahedral symmetry is possible.

I desire to express my warmest thanks to Prof. Sir William Bragg for his encouragement and helpful interest. I am also indebted for their advice and criticism to my colleagues at the Davy Faraday Laboratory, especially to Dr. Müller. The work was carried out during my tenure of the Hertha Ayrton Fellowship, and I wish to thank both the Council of Girton College and the Management of the Royal Institution for financial assistance. My thanks are, moreover, due to Prof. J. F. Thorpe and Prof. C. K. Ingold, through whose kindness a pure sample of pentaerythritol tetra-acetate was prepared for me in the Organic Chemical Laboratory of the Imperial College of Science and Technology.

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# *Investigations on the Scattering of Light in Colloidal Solutions and Gels. Part* I—*Agar Sol and Gel.*

By K. KRISHNAMURTI.

(Communicated by F. G. Donnan, F.R.S.—Received August 1, 1928.)

## *Introduction.*

One of the fundamental problems in the field of colloids is the investigation of their structure. This is a subject of considerable importance and has been attracting a great deal of attention from workers in this field. A systematic study of the various physical properties of colloids is essential for a clear understanding of the nature of the colloidal state. The optical properties are of special importance as they have the great advantage of revealing the structure of colloidal systems without disturbing their internal equilibrium. They furnish direct information concerning the size and the shape of the colloidal particles.

In a series of papers, of which this is the first, the author proposes to publish investigations on the scattering of light in colloidal solutions and gels. An attempt will be made to discuss the various problems concerning their structure, as revealed by the study of the Tyndall effect in such systems.

The ultra-microscope is extremely useful, where it can be used, in revealing the actual state of particles in the sols and gels. But, it cannot be applied in the investigation of all sols, as it has certain limitations, viz., when the particles have diameters of the same order of magnitude as the wave-length of light, the strong light reflected from the big particles masks the Tyndall light of the smaller particles. On the other hand, when the particles are too small to be optically resolved, or too numerous as in concentrated sols, or when the difference between the refractive indices of the particles and the dispersion medium is not appreciable, we observe only a uniform illumination of the field, instead of separate diffraction images of the particles. Further, in ultramicroscopic investigation, it is not possible to control the external conditions, such as temperature, etc.

But, the observations of the light-scattering in colloids—whether lyophilic or lyophobic—suffer no such limitations, and hence are well suited for investigations of colloids and gels under different conditions.

The first important investigations in this field were those of Lord Rayleigh, who developed a theory to explain the observed scattering of light in transparent colloids. The mathematical expression* he derived was

$$\mathrm{I} = \frac{9\nu\pi^2 v^2 \mathrm{A}^2}{\lambda^4 x^2} \cdot \left(\frac{n_1^2 - n_2^2}{n_1^2 + 2n_2^2}\right)^2 \cdot \mathrm{Sin}^2\,\theta. \tag{1}$$

where

I is the intensity of the scattered light, at a distance $x$ from the scattering particle.

$v$ the volume of the scattering particle.

$\nu$ the number of particles contained in unit volume.

$\lambda$ and A the wave-length and the amplitude of the incident light.

$n_1$ and $n_2$ the refractive indices of the particle and the dispersion medium.

$\theta$ the angle between the incident and diffracted beams.

If we consider the intensity of the light scattered at right-angles to the incident beam, the above expression reduces to

$$\mathrm{I} = \frac{9\nu\pi^2 v^2 \mathrm{A}^2}{\lambda^4 x^2}\left(\frac{n_1^2 - n_2^2}{n_1^2 + 2n_2^2}\right)^2. \tag{2}$$

From this formula it will be seen that the intensity of the scattered light is proportional to the number of particles per unit volume, and to the square of the volume of the particle, and it also depends upon the refractive indices of the dispersion medium and the particles.

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* H. Freundlich, 'Colloid and Capillary Chemistry,' p. 381 (1926).

Formula (2) can be written as

$$I = k \, . \, \nu \, . \, v^2/\lambda^4, \tag{3}$$

where $k$ is a constant.

The concentration of a colloidal solution is given by

$$c = \nu \, . \, v \, . \, \rho. \tag{4}$$

where $\rho$ is the density of the particles.

Introducing this into formula (3) we have

$$I = k \, . \, cv/\rho\lambda^4. \tag{5}$$

Now for sols of the same concentration, but of varying particle size, we see that the intensity of the scattered light is proportional to the volume of the particle. ($\lambda$ will be a constant if we use the same source of light throughout.)

On the other hand for sols containing particles of uniform size, but of different concentrations, the intensity of the scattered light is proportional to the concentration.

The above expressions relate to the case where the particles are many times smaller than the wave-length of light and are optically isotropic and distributed at random. They hold good only in the case of dilute colloidal solutions containing very small colloidal particles. In concentrated sols, the assumption of random distribution of the particles can no longer be true. If the particles are big, the intensity of the scattered light is not a simple function of the square of the volume of the particle, but is a much more complicated one. Besides, it has been shown that the particles in several metallic colloids are not optically isotropic. Hence, the expressions derived by Rayleigh are limited in application.

Rayleigh's theory also leads to the result that the scattered light will be completely polarised in a direction perpendicular to the incident beam. This is approximately true in some colloidal solutions. But, in the case of many others, the distribution of the scattered light about the planes perpendicular to the incident beam, as indicated by Rayleigh's theory, is no longer symmetrical. Further, the polarisation is maximum in a direction which makes an angle considerably greater than 90° to the original beam, and here also the polarisation is incomplete. These facts indicate that the relations deduced by Rayleigh do not hold good for coarser particles.

Mie* studied the problem of the absorption and scattering of light by colloidal solutions containing particles of any dimensions. His theory relates to *spherical* particles, whose electrical conduction is not negligible. His main conclusions are as follows :—

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* 'Ann. Physik,' vol. 25, p. 377 (1908).

(1) The distribution of scattered energy corresponds to Rayleigh's formula so long as the particles are very small (of the order of 100 $\mu\mu$) ; and the beam scattered at an angle of 90° to the incident beam is completely plane polarised (never elliptically polarised).

(2) When the light scattered at right angles to the incident beam is not completely polarised, it follows that the colloidal solution contains particles of diameter over 100 $\mu\mu$.

(3) When the particles have diameters over 100 $\mu\mu$, the proportion of the unpolarised light in the scattered beam increases rapidly, and with particles of diameter 130 $\mu\mu$ the polarisation may be about 90 per cent.

(4) When the particles are of diameter over 100 $\mu\mu$, the direction of maximum polarisation of the scattered beam is displaced towards an angle greater than 90° from the incident beam, and with particles of size 160 to 180 $\mu\mu$, the maximum of polarisation lies about 110° to 120°.

(5) At constant concentration, the diffused light in very fine suspensions increases with the particle size, and is proportional to the volume of the particles.

(6) In the case of gold sols, which were studied in detail by Mie, the gold particles have a maximum of absorption in the green, and a maximum of reflection in the yellowish-red. Very small particles absorb light strongly and reflect weakly, and hence the red colour of the fine grained gold sols. With larger particles reflection becomes more predominant, and the maximum of absorption is much flatter and is displaced towards the red side of the spectrum, and hence the blue colour of coarse-grained gold sols.

Steubung observed that blue gold sols can also be obtained with very small particles—a fact which contradicts Mie's theory. Gans* has obtained agreement with Mie's theory as well as Steubung's results by assuming that the particles may be ellipsoidal in form. The mathematical calculation of such a problem is very difficult ; and Gans has endeavoured to solve it by confining himself to particles whose linear dimensions are small compared to the wavelength of light. His main results may be summarised as follows :—

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* 'Ann. Physik,' vol. 37, p. 881 (1912), vol. 47, p. 270 (1915), vol. 62, p. 331 (1920) ; 'Z. Physik,' vol. 17, p. 353 (1923), vol. 30, p. 231 (1924).

(1) The appearance of the absorption curve depends very greatly on the shape of the particles.

(2) From the spectrophotometric observations of Steubung it could be concluded that, in general, the shape of the particles does not deviate very much from the spherical form; but the observations of polarisation show that the particles must deviate a little from the spherical form.

(3) The light scattered sideways from a colloidal solution is completely plane-polarised when the particles are spherical; it is partly depolarised when the shape of the particles is different. The extent of depolarisation is greater, the more the shape of the particles deviates from the spherical form. Hence, the measurements of the depolarisation of the scattered light is a means of determining the shape of the particles.

(4) The smaller the particles, the more complete is the polarisation of the scattered light, and the coarser they are, the greater is the depolarisation.

W. Schoulejkin* has shown that, with colloidal particles whose diameter is approximately equal to the wave-length of light, the law of scattered radiation is very different from that of small particles, as given by Rayleigh's formula. The polarisation is also in a different plane; and the maximum of polarisation is displaced towards angles greater than 90° and even here it is not complete. In the case of very big particles reflection takes place. There is thus a continuous change from scattering (diffraction) of light to reflection as we pass from very small to very big colloidal particles.

It will thus be seen that the study of the intensity and depolarisation (*i.e.*, the ratio of the unpolarised to the polarised light) will give valuable information regarding the size and shape of the colloidal particles. The object of the present investigation is to gain insight into the formation of colloidal solutions and gels and other problems connected with their structure by a systematic study of the light-scattering in such systems. In this paper the results obtained with agar sols and gels will be described and their bearing on the theory of gel-structure discussed. Agar sols have been selected for work, because they can be rendered very clear and transparent by filtration, they set to gels even at very low concentrations, and further it is possible to obtain the same agar solution both in the sol and the gel states at the same temperature.

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* 'Phil. Mag.,' vol. 48, p. 307 (1924).

## EXPERIMENTAL.

### *Measurement of the Relative Intensity of the Scattered Light.*

The apparatus used for the measurement of the relative intensity of the light scattered by the colloidal solutions is described below and shown in fig. 1.

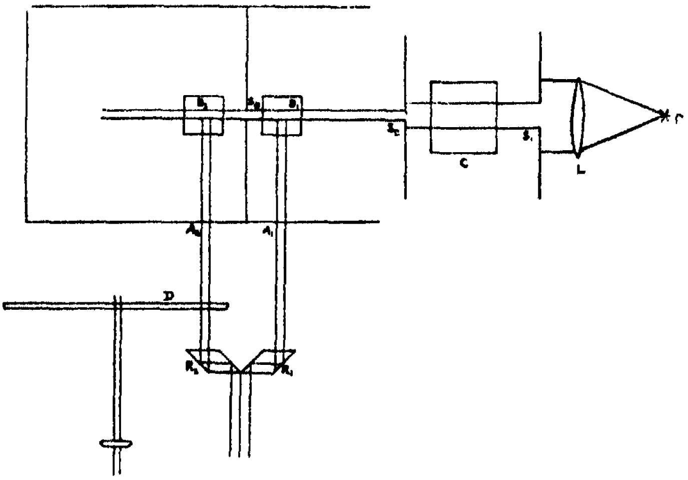

FIG. 1.

P is the tungsten arc of a pointolite lamp (1000 candle power) enclosed in a big wooden box which is painted inside and out with non-reflecting black. The intense white light is rendered nearly parallel by the lens L. This is done by focussing the arc on a distant screen or wall. C is a cell with plane parallel faces, containing cold distilled water, which is used to remove the heat rays from the beam of light. (It has been shown that cold water is quite as efficient as alum solution in absorbing heat rays, and it has the advantage that it does not become turbid after long continued use, *cf.* Coblenz, Carnegie Institute Publications, Part VI, p. 47 (1908).

$S_1$, $S_2$, $S_3$ are three circular slits placed in the path of the incident beam so as to cut off the stray light.

This arrangement gives an intense, steady parallel beam of light, which passes through the bottle $B_1$ containing the liquid standard for comparison and then through the bottle $B_2$ containing the colloidal solution for examination. The bottle $B_2$ is immersed in a tank with a metal frame fitted with four plates of good glass, which have been tested and found to be free from optical defects. Some convenient liquid (usually water) is poured into this tank to serve as a bath, and is maintained at a definite temperature. The bottles $B_1$ and $B_2$ are rectangular and have parallel sides. They are painted with dull black except in certain positions on the sides for the passage of the incident and scattered beams of light. This is to secure a dark background against which the scattered light may be observed. The beams of light scattered at right angles to the incident beam by the liquid standard and the colloidal solution are viewed through two small rectangular apertures $A_1$ and $A_2$ (about 6 mm. × 4 mm.) and are matched in intensity by means of the Abney rotating sector photometer D, in which the angle of the sector could be varied during its rotation.

Some of the important conditions for accurate photometry are :—

(1) The patches of light to be compared should be equal in area.

(2) They should be contiguous, so that the line of separation between the two may disappear when the match is perfect.

(3) The two patches should be of the same colour.

The first of these conditions is satisfied by making the apertures $A_1$ and $A_2$ equal in area. The second is fulfilled by the following device :

The scattered beams of light from the liquid and the colloidal solution are initially separated by about 1·5 inches, so that accurate matching is almost impossible. They are brought together so as to be adjacent by interposing in the path of the beams two optical rhombs $R_1$ and $R_2$, which, when placed in a certain position (to be ascertained by trial), cause the two parallel scattered beams to suffer total reflection twice at right angles, so that they finally emerge as two parallel beams adjacent to each other.

The two optical rhombs are of the same material and dimensions, so that the diminution in intensity suffered by the two scattered beams while passing through the rhombs is the same, and hence the ratio of their intensities remains unaltered.

The third condition is satisfied (if the tint of the scattered beam from the sol differs from that of the liquid standard) by introducing a suitable colour filter (usually a Wratten photometric blue filter) in the path of the former beam.

The light scattered by some of the sols and many of the gels is much more intense than the faint bluish light scattered by the liquid standard. Hence to facilitate comparison, a neutral tint filter (or photometric blue filter) of the required density is placed in the path of the beam scattered by the colloidal solution or gel.

It is also essential for accurate photometry to prevent any stray light from affecting the eyes of the experimenter. With this object, the rotating sector and the support for the optical rhombs are enclosed in a box, painted with non-reflecting black, and open on one side, through which the observations are made, while the opposite side has two apertures through which the two scattered beams enter the "observation box."

The readings were taken when the eye had become accustomed to the darkness of the room. This generally takes a few minutes. The readings obtained were quite reproducible.

### *Measurement of the Depolarisation of the Scattered Light.*

The degree of depolarisation of the scattered light is determined by means of the apparatus shown in fig. 2, and described below.

The scattered light is observed through a double image Wollaston prism W, which gives two images whose intensities are in the same ratio as the polarised components of the scattered light. These two images are equalised in intensity by rotating the nicol N, which is mounted in a brass tube T. Attached to the tube T is a pointer P, the free end of which moves round a circular scale graduated in degrees. As the nicol is rotated two positions can be found in which the images appear to be of equal intensity. If the angle between the two positions of the nicol be $2\alpha$, then the ratio of the intensities of the weak component to the strong component of the scattered light is given by $\tan^2 \alpha$. This gives the depolarisation factor $\theta$ of the scattered light.

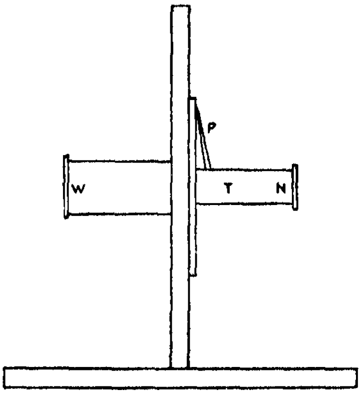

FIG. 2.

Using this apparatus the extent of polarisation of the scattered light in a direction perpendicular to the incident beam was determined. A set of readings was obtained and their average taken as the final value.

### *Standards used for Comparison of the Intensity of the Light Scattered by the Colloidal Solutions and Gels.*

The relative intensity of the light scattered by the colloids is determined by comparing it with the light scattered by a standard. Previous workers on the Tyndall effect in colloids used colloidal suspensions as standards for comparison. Several such standards have been tried by the author, and found to be unsatisfactory, as there was always the uncertainty of obtaining exactly reproducible suspensions. If the suspensions are coarse, they settle down in course of time, or in the case of finely-dispersed colloids a steady change takes place from day to day due to ageing. Further, with the arrangement used for measuring the intensity, it is not possible to use any colloid or coarse suspension, as this cuts down a good portion of the incident beam of light before this enters the colloid to be examined. Considering all these difficulties, it was thought best to use a liquid as a standard. The advantages of using this are :—

(1) The liquid undergoes no change whatsoever even after a considerable length of time.

(2) The light scattered by the liquid, being truly molecular, is the same in all samples of the particular liquid, provided it is pure and dust free.

(3) It can be obtained in a pure condition and rendered dust free by distillation *in vacuo.*

(4) The intensity of the light passing through is very little affected by the liquid.

Carbon-bisulphide has been found very suitable as a standard, since the light scattered by this liquid is quite considerable compared to other liquids. But when the light scattered by the sol is very feeble, benzene has been used instead. These liquids could be rendered dust free by distillation *in vacuo* without ebullition.

*Preparation of the Agar Sols.*—A weighed quantity of pure agar (with an ash content of 2·1 per cent.) in the form of fine powder, is stirred with the required amount of conductivity water in an Erlenmeyer flask. This is gradually brought up to boiling with frequent stirring, and is then heated slowly for a few minutes longer. The water lost by evaporation is made up approximately by the addition of the requisite amount of water. The sols so obtained are turbid, and are therefore not suitable for the measurement of light-scattering. They are rendered quite clear by filtering through a filter paper, the filter funnel being placed in a hot water funnel. The filtrate is collected in the bottle (used for the measurement) which is immersed in hot water, so that the sol may not set to a gel. The filtration is extremely tedious in the case of sols of more than 1 per cent. concentration.

## RESULTS AND DISCUSSION.

### 1. *Effect of Temperature on the Light-scattering of Agar Sols and Gels.*

When an agar sol of as low a concentration as 0·5 per cent. is cooled to 35° C. it sets to a gel. On heating it "liquefies" again, but not until a temperature of about 90° is reached. Below 90° the gel does not liquefy however long it may be maintained at that temperature. These sols thus show a marked hysteresis. This fact enables us to obtain them either in a sol or gel condition at any temperature between 35° and 90° C.

*Sol-Gel Transformation.*—During the transformation of an agar sol to a gel, a change in several properties of the system occurs; for example, the viscosity increases, the clear sol becomes opalescent, and it acquires elastic properties which were initially absent in the sol state. The property which has been hitherto investigated in great detail by previous workers during the sol-gel transformation is the viscosity. A completely continuous change has been observed during this transition. But the viscosity measurements are very unreliable during the process of setting, and hence cannot help us to gain an insight into the mechanism of gel-formation.

As pointed out in the introduction, the measurements of light-scattering have the great advantage of revealing the delicate changes in the system without disturbing it. The following investigation deals with the variation in the intensity and depolarisation of the light scattered by agar sols during the transition into the gel state. It was possible to ascertain the nature of this change, at what temperature it commences, and whether gelatinisation is a continuous process or not. The following table gives the results of the measurements of the intensity and depolarisation of the light scattered by a 1 per cent. agar sol at different temperatures ranging from 80° to 25° C. The results obtained are significant in relation to the problem of gelatinisation. The figures in column (2) express the ratios of the intensity of the light scattered by the agar sol to that of the liquid standard, viz., carbon bisulphide. (These are also called the "Tyndall numbers.") Those in column (3) give the depolarisation factor $\theta$, which is the ratio of the intensity of the weak component to that of the strong component in the scattered light.

It will be seen from the results in Table I that—

(1) The light-scattering capacity of the agar sol does not undergo any appreciable change as it is cooled from 80° to 40°. A steady rise in the intensity of the scattered light begins at about 35° C., and below this temperature the Tyndall number increases rapidly. The sol sets to a gel at about 33°, when

the Tyndall number is 35. In fact, even at 35° it is possible to obtain a gel by keeping the sol at this temperature for some time.

Table I.

| Temperature. | Intensity ($CS_2 = 1$). | Depolarisation factor. |
|---|---|---|
| ° | | Per cent. |
| 75 | 10·5 | 7·2 |
| 70 | 10·5 | 7·2 |
| 60 | 10·6 | 7·2 |
| 50 | 10·6 | 7·2 |
| 40 | 10·9 | 7·2 |
| 35 | 14·0 | 7·2 |
| 33 | 35·2 | 7·2 |
| 31 | 44·0 | 6·2 |
| 30 | 60·7 | 8·2 |
| 29 | 70·4 | 9·4 |
| 27 | 88·0 | 10·6 |
| 25 | 98·2 | 12·3 |
| 18 | 110·0 | 16·3 |

(2) The increase in light-scattering commences before the actual gelation and it continues to increase long after the whole system has set to a rigid gel. There is no abrupt change just at the point of gelation.

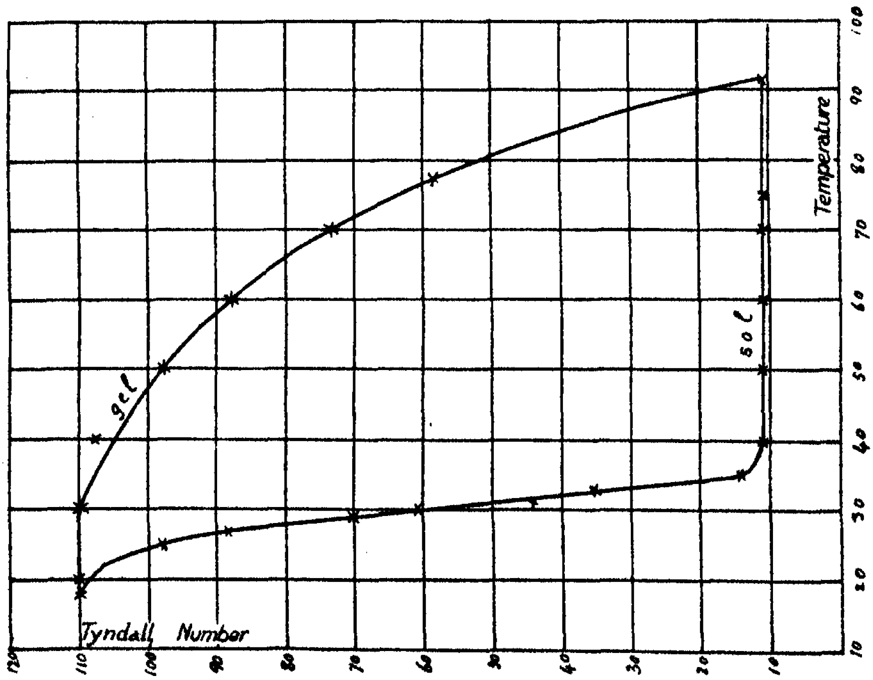

FIG. 3.

The variation of the Tyndall number with temperature is shown in fig. 3. It will be noticed that at about 35° there is a marked change in the direction of the temperature—Tyndall number curve. At about 20° the change in the intensity of the scattered light is slow, but a constant value is not reached until the temperature is about 18° C.

(3) There is also a marked change in the depolarisation factor $\theta$ of the scattered light during the sol-gel transformation. As the sol is cooled from 80° the depolarisation remains unchanged until a temperature of 35° C. is reached. At about 31° a small but perceptible decrease in $\theta$ is observed, and below this temperature the depolarisation steadily increases till about 18°, when a constant value is attained.

(4) The change in depolarisation is observed after the intensity of the scattered light has increased appreciably.

*Discussion.*—An increase in the number of colloidal particles or their size will be indicated by an increase in the intensity of the scattered light. It will therefore be seen from Table I that, until a temperature of 35° is reached, there is no indication of any change in the colloidal particles. But at 35° a steady increase in the Tyndall number commences, which may mean that either fresh colloidal particles are being formed or their size is increasing, or both. It will also be noticed that the change in the depolarisation factor $\theta$ is not appreciable until a lower temperature is reached.

A change in the depolarisation can, in the present case, be brought about by the following factors :—

(1) An increase in the size of the particles, which has the effect of increasing the proportion of unpolarised light in the Tyndall cone, and hence the depolarisation factor.

(2) A change in the spherical symmetry of the particles. An increase in spherical symmetry tends to decrease the depolarisation factor of the scattered light, while a departure from it causes $\theta$ to increase.

A mere increase in particle size increases $\theta$, but if this tends to the formation of particles which have greater spherical symmetry than the original colloidal particles, $\theta$ decreases. Thus, these two factors act in opposite directions. The actual effect observed, viz., that at first the depolarisation factor decreases slightly till 31°, and then steadily increases, depends upon which of the two factors is more appreciable. In the case of a 0·2 per cent. agar sol the depolarisation factor decreases very markedly while the intensity I increases. A decrease in $\theta$ cannot here be due to a diminution in particle size during gelation, since such a view is contradictory to ordinary experience, and since, what is more important, the intensity of the scattered light increases steadily during gelation. Hence, the only possible explanation of the decrease in the depolarisation of the scattered light as its intensity increases is that the colloidal particles, while they increase in size, become more spherical at the same time. In the earlier stages of the growth of the particles the increase in their spherical symmetry is very pronounced, and hence 0 tends to decrease. But below 30° we find that the depolarisation increases with the intensity, thereby indicating that an increase in the size of the colloidal particles or their aggregates is of importance in determining the depolarisation of the scattered light. This is probably true to a greater extent at still lower temperatures when the particles apparently suffer no further alteration in shape.

The question naturally arises whether the agar sols above 40° are molecularly dispersed or contain colloidal particles. The method of preparation shows that the dispersion of agar in water can be brought about by heating. It seems probable that the important factor which causes this dispersion is the strong affinity of the agar micelles for water. The water tries to penetrate through the pores of the solid agar, and causes it to be split up into separate micelles. The higher the temperature, the greater the facility with which this subdivision of agar takes place. When the whole process is completed we get a dispersion in which each micelle is surrounded by a hydration layer. These micelles need not all be of the same type ; some may be monomolecular and others polymolecular. In other words, part of the agar is probably in the molecularly dispersed condition and the rest in the form of colloidal micelles. The strong Tyndall cone from the agar sols of 1 per cent. concentration or more is a sure indication that part of the substance must be present in the colloidally dispersed condition.

On the other hand, in weak sols of about 0·2 per cent. concentration, the agar is molecularly dispersed to a large extent, as shown by the very low light-scattering capacity of such sols. Thus the colloidal content increases with the concentration of the sol.

It, therefore, seems very probable that an agar sol is a colloid having as its intermicellary liquid a molecular solution of agar. When the sol is cooled, the hydration of the colloidal particles increases very appreciably, thereby reducing the amount of "free water" in the intermicellary solution. This, together with the decrease in solubility of agar due to a lowering of temperature causes the intermicellary liquid to become supersaturated. As a result, fresh colloidal particles will be formed, and when these are sufficiently numerous, the further supersaturation will be relieved by the condensation of the dissolved agar on the particles already present in the sol. This brings about an increase in the size of the particles, and also tends to make them more spherical in shape. The phenomenon of gel-formation is essentially due to the union of the hydrated particles, enmeshing the intermicellary liquid. This confers on the system the rigidity which is characteristic of a gel. The coalescence of the hydrated particles takes place altogether independently of their growth in size, and hence there is no sudden change in the light-scattering during the process of gelation.

That at first fresh particles are formed is shown by the fact that the intensity of the scattered light increases while the depolarisation remains constant for some time. For mere increase in the number of colloidal particles has no marked effect on the depolarisation factor. This follows from the fact that agar sols of different concentrations above 40° all exhibit the same depolarisation though the intensity of the scattered light varies. The subsequent increase in the size of the particles is indicated by the change in the depolarisation factor as the Tyndall number increases.

*Gel-Sol Transformation.*—By heating an agar gel to a temperature of about 90° it can be converted into a sol, which has exactly the same light-scattering capacity as the original sol. It is a matter of interest to determine whether the change in light-scattering during the gel-sol transformation is continuous or abrupt. Table II contains results for the intensity and depolarisation of the light scattered by a 1 per cent. agar gel at different temperatures during its conversion into a sol.

Table II.

| Temperature. | Intensity ($CS_2 = 1$). | Depolarisation factor. |
|---|---|---|
| ° | | Per cent. |
| 15 | 110·0 | 16·0 |
| 20 | 110·0 | 16·0 |
| 30 | 110·0 | 16·0 |
| 40 | 107·4 | 15·5 |
| 50 | 97·7 | 14·0 |
| 60 | 88·0 | 11·2 |
| 70 | 73·5 | 9·7 |
| 75–80 | 58·5 | — |

It will be seen from the above data that the light-scattering of the agar gel does not undergo any appreciable change till about 40° ; but if the temperature be raised about 40°, both the depolarisation and intensity of the scattered light gradually decrease. This indicates that though the gel remains quite rigid till about 90°, the colloidal micelles which form the gel undergo a continuous change in size—they become smaller.

It has been shown from the measurements of relative viscosity as well as the light-scattering of a 0·5 per cent. agar sol at different temperatures, that the hydration of the colloidal particles increases with a lowering of temperature. It is obvious that an increase in temperature will have the reverse effect, viz., to decrease the water of hydration, *i.e.*, the amount of water present in the intermicellary liquid in the gel increases with the temperature. Hence, more of agar diffuses from the "gel micelles" into the intermicellary liquid, thus causing the agar particles to decrease in size.

The fact that the gel remains quite rigid even at a temperature which is much higher than the "setting point," suggests that the particles in the gel are linked together to form a structure. As shown above, these particles become smaller with increasing temperature, until finally the forces holding them together become so feeble that they fall apart. This results in the "melting" of a gel.

The following experiments provide quite definite evidence in support of the above view. When a dilute agar sol is shaken with enough alcohol the sol becomes very turbid, due to the precipitation of agar in the form of fine particles. If, on the other hand, a weak gel of 0·2·per cent. concentration be similarly treated, the gel-micelles become dehydrated and separate out as coarse flocculi, which settle down after a time.

Again, on gradually cooling a 1 per cent. agar sol a homogeneous gel will be formed; but, if the cooling be not uniform throughout the sol, flocculi separate out at the "setting point." These observations evidently show that the micelles present in the gel are much coarser than those in the original sol, and that they are linked together.

### *Comparison of the Scattering of Light in Agar Sols and Gels at the same Temperature.*

Even a superficial examination of agar sols and gels of the same concentration and at the same temperature reveals that the gels are more opalescent than the sols. In Table III the results of light-scattering obtained with 1 per cent. agar sol and gel at the same temperature are given. At all the temperatures ranging from 40° to 70° the measurements are made after equilibrium has been attained: *i.e.*, no further change in the Tyndall number is noticed even after keeping it for several hours.

Table III.

| Temperature. | Intensity of scattered light in sol state. | Intensity of scattered light in gel state. | Ratio. |
|---|---|---|---|
| ° | | | |
| 70 | 10·5 | 73·5 | 7·0 |
| 60 | 10·6 | 88·0 | 8·3 |
| 50 | 10·6 | 97·7 | 9·2 |
| 40 | 10·9 | 107·4 | 9·9 |

A comparison of the Tyndall number in the sol and gel states shows that, at all the temperatures, the gel scatters more light than the sol. It will also be noticed that, with increasing temperature, the difference between the sol and gel tends to diminish.

Hatschek and Humphrey* found that the conductivity of an agar gel containing copper sulphate was about 2 per cent. greater than that of the corresponding sol at the same temperature. This difference could not possibly have been due to any experimental error. Hatschek's explanation is that gelation is the segregation of a phase much richer and an aqueous phase much poorer in agar than the sol, so that the aqueous phase which is supposed to carry most of the current offers less resistance than the more viscous sol. Von Weimarn, on the other hand, attributes this difference in conductivity to an aggregation of the colloidal particles, and the consequent desorption of the electrolytes by the agar.

It is evident that the increase in conductivity in the gel state must be due to some factor which increases the concentration of the electrolyte in the intermicellary liquid. It appears very probable that this factor is the capacity of the agar particles to adsorb water in preference to the electrolytes, so that the distribution ratio of the electrolyte (copper sulphate in the present case) between the intermicellary liquid and the adsorbed water is greater than one. This explanation is based on the view regarding the nature of gelation, which has been suggested in a previous section.

### *Variation of the Intensity of the Scattered Light with the Concentration of the Sol.*

The light-scattering capacity of a sol depends upon its concentration. The results showing the variation of the intensity of the scattered light with the concentration of agar sols at different temperatures are given in Tables IV and V. The sols were all prepared in the same manner and filtered to render them clear and transparent. It was found very difficult to obtain sols of more than 2 per cent. concentration, as the filtration of such sols is an extremely tedious process.

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* 'Trans. Faraday Soc.,' vol. 20, p. 18 (1924).

Table IV.—Sol State.

| Concentration. | Intensity of scattered light ($CS_2$ = 1). | | | |
|---|---|---|---|---|
| | 60°. | 50°. | 40°. | 35°. |
| Per cent. | | | | |
| 0·2 | 2·6 | 2·6 | 2·5 | 2·6 |
| 0·5 | 6·7 | 6·5 | 6·5 | 6·5 |
| 1·0 | 10·6 | 10·6 | 10·9 | 14·0 |
| 2·0 | 13·5 | 13·5 | 14·7 | 19·0 |

Table V.—Gel State.

| Concentration. | Intensity of scattered light ($CS_2$ = 1). | | | | |
|---|---|---|---|---|---|
| | 60°. | 50°. | 40°. | 30°. | 20°. |
| Per cent. | | | | | |
| 0·2 | 12·8 | 13·8 | 14·7 | 16·3 | 16·3 |
| 0·5 | 46·8 | 53·3 | 53·3 | 55·0 | 55·0 |
| 1·0 | 88·0 | 97·7 | 107·4 | 110·0 | 110·0 |
| 2·0 | 176·0 | 220·0 | 220·0 | 220·0 | 220·0 |

On considering the results given in Table IV it will be seen that the intensity of the scattered light in the sol state is proportional to the concentration of the sol in the case of 0·2 per cent. and 0·5 per cent. sols. With sols of higher concentration the Tyndall number does not increase proportionately, *i.e.*, the ratio $\frac{\text{Tyndall number}}{\text{concentration}}$ falls off gradually.

From Table V it will be seen that in the case of 0·5 per cent., 1·0 per cent. and 2 per cent. agar gels, the intensity of the scattered light, especially at lower temperatures, is proportional to the concentration, whereas in the 0·2 per cent. gel it is comparatively less.

It will be interesting to notice that the ratio of the Tyndall number (I) in the gel and sol states increases with the concentration.

The results are given in Table VI.

Table VI.

| Concentration per cent. | 0·2 | 0·5 | 1·0 | 2·0 |
|---|---|---|---|---|
| I in gel : I in sol | 6·3 | 8·5 | 9·9 | 15·0 |

The regular increase of the ratio given in column 2 evidently means that the micelles in the concentrated gels are bigger and more numerous than in the dilute ones. The formation of bigger micelles in gels has been attributed, in a previous section, to the supersaturation in the sols brought about by cooling. It, therefore, follows from the above that the amount of molecularly dispersed agar is greater in the concentrated sols than in the dilute ones—a conclusion which is in complete accord with our expectations.

### *Variation of the Intensity of Scattered Light with Time.*

The light-scattering capacity of an agar sol above 40° does not undergo any change even on allowing it to stand at that temperature for a long time. But, at and below 35°, the intensity of the scattered light increases with time, until finally a constant value is reached. The time required for such an equilibrium value to be reached depends upon the temperature—the lower the temperature the more rapid the change, a fact which is clearly illustrated by the results in Table VII, which show the variation of Tyndall number with time.

Table VII.

Agar Sol (1 per cent. concentration). Temperature 35°.

| Time. | Tyndall number. | Time. | Tyndall number. |
|---|---|---|---|
| Minutes. | | Minutes. | |
| 0 | 11·0 | 60 | 31·4 |
| 5 | 12·6 | 70 | 36·7 |
| 15 | 13·3 | 80 | 40·0 |
| 20 | 15·2 | 100 | 47·6 |
| 30 | 20·0 | 250 | 65·2 |
| 40 | 24·4 | After 21½ hours | 92·6 |
| 50 | 27·5 | | |

Agar Sol (1 per cent. concentration). Temperature 30°.

| Time. | Tyndall number. | Time. | Tyndall number. |
|---|---|---|---|
| Minutes. | | Minutes. | |
| 0 | 11·0 | 21 | 58·7 |
| 5 | 12·1 | 25 | 67·7 |
| 10 | 23·2 | 40 | 73·3 |
| 13 | 26·7 | 45 | 76·5 |
| 15 | 36·7 | 60 | 88·0 |
| 18 | 48·9 | 120 | 92·6 |

It can be seen that the time taken for a value of Tyndall number (say, about 100) to be reached at 35° is very long (more than 24 hours); whereas this value is attained in less than half-an-hour at 25°. This observation is in harmony with the explanation given above, that the increase in particle size during gelation depends upon the supersaturation existing in the solution. The lower the temperature the greater the supersaturation, and hence the more rapid is the precipitation of the molecularly dispersed agar.

The rate of increase of the Tyndall number with time also depends upon the concentration of the sol, as is brought out clearly by the results in Table VIII. The Tyndall numbers of agar sols of different concentrations are compared at definite intervals of time, and the relative increase in each case indicated in the last column.

Table VIII.

Temperature 35°.

| Concentration. | Tyndall number at different intervals (I). | | | | | Relative increase in I in 60 mins. |
|---|---|---|---|---|---|---|
| | 0 mins. | 15 mins. | 30 mins. | 40 mins. | 60 mins. | |
| Per cent. | | | | | | Times. |
| 2·0 | 19·1 | 44·0 | 53·3 | 70·4 | 80·0 | 4·2 |
| 1·0 | 11·0 | 13·3 | 20·0 | 24·4 | 31·4 | 2·9 |
| 0·5 | 6·5 | 7·5 | 8·2 | 9·0 | 10·1 | 1·6 |

It will be noticed that, as the concentration of the sol increases, the Tyndall number increases more and more rapidly. This is obviously due to the fact that the amount of the molecularly dispersed agar is greater in the more concentrated sols than in the dilute ones, and hence the supersaturation brought about by cooling is correspondingly higher. This results in the precipitation of more of agar from the sol.

In all the cases referred to above, the increase in Tyndall number with time is quite continuous, *i.e.*, there is no sudden change of direction in the time-Tyndall number curve (fig. 4). This indicates that the growth of the colloidal micelles takes place altogether independently of gelation.

It is a matter of interest to ascertain, if the sudden cooling of an agar sol might result in the formation of a gel, without any alteration in the light-scattering capacity. Attempts have been made to examine how far this expectation is fulfilled. Sometimes the sudden cooling led to the formation of a heterogeneous gel which was turbid, and, when examined under strong

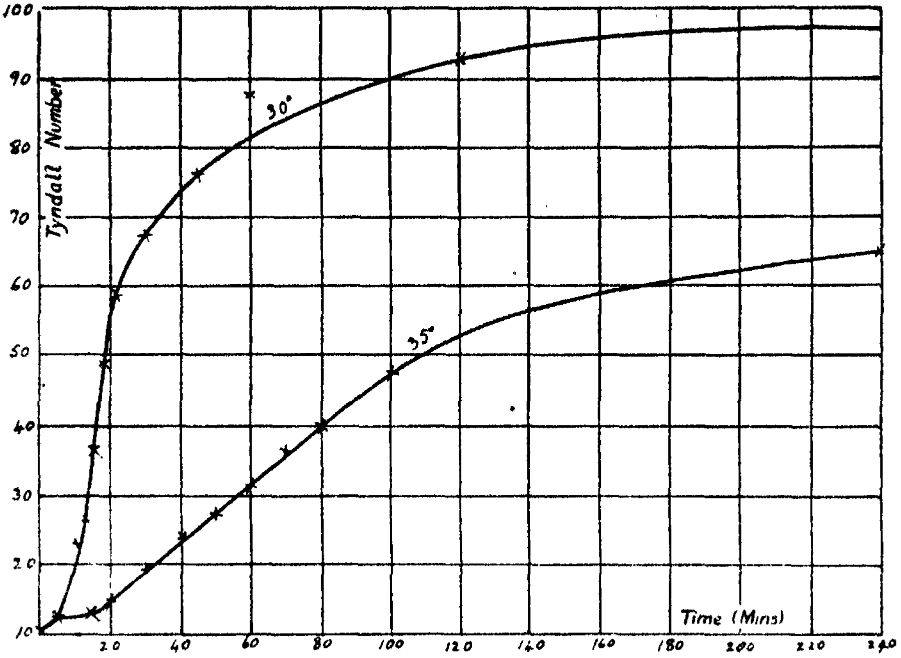

FIG. 4.

illumination, showed the presence of separate flocculi. But, whenever it was possible to obtain a clear homogeneous gel by sudden cooling, it was noticed that the intensity of the scattered light was distinctly higher than in the sol state. Thus, it was not possible to obtain agar gels, the micelles in which were identical in number and size with those in the original sol.

### *Variation of the Depolarisation of the Scattered Light with Temperature and Concentration.*

It has already been shown that the intensity of the light scattered by an agar sol remains practically unchanged as it is cooled from 80° to 40°; but at and below 35° the intensity rapidly increases. Besides the change in the intensity, the depolarisation factor of the scattered light also varies below 35°, this variation being different in sols of different concentration. The results obtained with agar sols of 2 per cent., 1 per cent., 0·5 per cent. and 0·2 per cent. concentrations at various temperatures are given in Tables IX, X, XI and XII.

Table IX.—2 per cent. Agar Sol.

| Temperature. | Depolarisation factor. |
|---|---|
| ° | Per cent. |
| 60 | 8·2 |
| 50 | 8·2 |
| 40 | 8·2 |
| 35 | 8·2 |
| 33 | 8·2 |
| 31 | 10·6 |
| 28 | 13·9 |
| 15° after several hours ………… | 21·7 |

Table X.—1 per cent. Agar Sol.

| Temperature. | Depolarisation factor. |
|---|---|
| ° | Per cent. |
| 60 | 7·2 |
| 50 | 7·2 |
| 40 | 7·2 |
| 35 | 7·2 |
| 33 | 7·2 |
| 31 | 6·2 |
| 30 | 8·2 |
| 29 | 9·4 |
| 27 | 10·6 |
| 25 | 12·3 |
| 18 | 16·3 |

Table XI.—0·5 per cent. Agar Sol.

| Temperature. | Depolarisation factor. |
|---|---|
| ° | Per cent. |
| 60 | 7·2 |
| 50 | 7·2 |
| 40 | 7·2 |
| 35 | 7·2 |
| 32 | 7·2 |
| 30 | 6·2 |
| 28 | 5·3 |
| 25 | 4·9 |
| 20 | 4·9 |
| 10° after several hours …………… | 7·2 |

Table XII.—0·2 per cent. Agar Sol.

| Temperature. | Depolarisation factor. |
|---|---|
| ° | Per cent. |
| 60 | 7·2 |
| 50 | 7·2 |
| 40 | 7·2 |
| 35 | 7·2 |
| 32 | 7·2 |
| 30 | 6·2 |
| 28 | 5·8 |
| 10° after several hours …………… | 3·8 |

In the case of the 2 per cent. sol we observe a regular increase in θ as the temperature is lowered below 32° until finally, after keeping the sol for several hours at about 15°, the value of θ rises to as much as 21·7 per cent. With a 1 per cent. sol there is a small but perceptible decrease in θ at first at about 32°, and below this temperature θ steadily increases, until finally at 18° the value is 16·3 per cent. This decrease in θ at first, followed by an increase, is more marked in the case of a 0·5 per cent. sol, whereas with 0·2 per cent. sol the value of θ gradually decreases. It is thus apparent that the higher the concentration of the sol, the greater the tendency of the depolarisation factor to increase. It is also interesting to notice that, in all cases, the change in the depolarisation factor commences long after the intensity of the scattered light has increased appreciably.

The following explanation is suggested for the above phenomenon:

At about 35° the supersaturation existing in the solution brings about the formation of fresh particles. The intensity of the scattered light, which is proportional to the number of particles in unit volume, consequently increases; whereas the depolarisation is not appreciably altered. This is followed by a condensation of the molecularly dispersed agar on the particles already present in the sol, thus increasing their size. The intensity of the scattered light therefore increases. But the change in the depolarisation factor is determined by the shape as well as the size of the particles. The larger the particles contained in the sol the greater is the depolarisation ($\theta$) of the scattered light; and the more they approach the spherical shape the less the value of $\theta$. It is probable that during the growth of particles, they tend to become more spherical due to the symmetrical condensation of agar on them. Thus $\theta$ is influenced simultaneously by two factors acting in opposite directions, and whichever is more appreciable will naturally have the greater effect. In the case of a dilute sol of 0·2 per cent. concentration, the increase in the size of the particles is slow and comparatively small, while their tendency to become spherical is more pronounced, hence $\theta$ decreases. But in the more concentrated sols the micelles grow to bigger dimensions, due to the precipitation of a large amount of agar, so that this factor has, evidently, the greater influence. Consequently $\theta$ increases as the temperature is lowered.

According to the theory, besides the shape and size of the colloidal particles, the concentration of the sol should also exert some influence on the depolarisation factor. This appears to be comparatively small, as is shown by the results in Table XIII.

Table XIII.

| Concentration. | $\theta$ in sol state. | $\theta$ in gel state. |
|---|---|---|
| Per cent. | Per cent. | Per cent. |
| 2·0 | 8·2 | 21·7 |
| 1·0 | 7·2 | 16·3 |
| 0·5 | 7·2 | 7·2 |
| 0·2 | 7·2 | 3·8 |

It will be seen that in the sol state $\theta$ does not vary appreciably with the concentration, whereas in the gel state the difference between the values of $\theta$ for the various concentrations is very marked. It is probable that this is due to the difference in size of the particles in the gels of different concentrations—the higher the concentration the bigger the particles.

### *Discussion of the Theory of Gel Structure.*

The problem of the structure of gels has received a great deal of attention for a long time past. In spite of the enormous amount of work done in this field, there still appear to be fundamental differences between the views of the different investigators.

Proctor,* Katz,† and others regard gels as one-phase systems, more or less solid-solutions. Such a theory seems to be very doubtful, since the particles constituting the gels are of bigger dimensions than those required by this theory, as shown by the strong Tyndall light in gels. Wo. Ostwald‡ considers them to be two-phase liquid-liquid systems, resembling emulsions. Hatschek§ finds this theory untenable, since the mechanical properties of such systems do not correspond with those of true gels.

The theory that gels are solid-liquid systems is generally considered to be the most satisfactory one. According to this view, gels consist of a network of the solid phase, in which the dispersion medium is enmeshed. Though this view is accepted by many of the investigators in its general form, there still appears to be a want of clear agreement as to the exact nature of the framework in gels, and the manner in which this is formed. The most important investigations in this field are those of Zsigmondy and his co-workers, whose ultramicroscopic investigations have greatly advanced our knowledge of the structure of gels. Zsigmondy's view is that the structure of gels is granular or flocculant, thus supporting Nägeli's original theory. The ultramicrons contained in the gels are assumed to be separated by thin layers of water surrounding them.

Zsigmondy and Bachmann have shown that, in addition to the grained structure as observed in gels of gelatin, agar, and silicic acid, some gels are fibrillar in structure. This was also noticed later by McBain and his co-workers in soap gels. As regards the exact nature of the solid phase in gels there has been a greal deal of discussion.

McBain,‖ from an exhaustive study of the different properties in soap sols and gels, has put forward the view that the colloidal particles in the sol and gel states are identical in nature and amount, so that gels differ from sols only in possessing elastic properties. Light-scattering measurements in agar sols and gels at the same temperature and also of sodium oleate solution in the sol and gel conditions, show that the intensity of the scattered light is greater in gels than in sols. This indicates that the particles in the gel state must be greater in number or size or both than in the sol state.

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* 'J. Chem. Soc.,' vol. 105, p. 313 (1914).

† 'Kolloidchem.,' Beihefte 9 (1917).

‡ "Theory and Practice of Colloid Chemistry," trans. by Fischer (1917), p. 103.

§ 'Trans. Faraday Soc.,' vol. 12, p. 17 (1916).

‖ 'J. Chem. Soc.,' vol. 117, p. 1506 (1920).

Further, the fact that there is a marked increase in the intensity of the scattered light, even before the agar sol sets to a gel, suggests that the colloidal particles originally present in the sol grow to bigger dimensions before the gel is formed. If this increase in the intensity of the scattered light were due to the aggregation of the micelles, there should be a sudden increase in light-scattering just at the point when the sol sets to a gel, and the Tyndall number should not vary any further after the formation of the gel. But actual experiments show that the Tyndall number increases before the gelation point (especially in the dilute sols) and this continues to increase long after the whole system has set to a gel.

Another observation which throws considerable light on the nature of the micelles in gels is that, if a dilute agar gel of 0·2 per cent. concentration be shaken vigorously so as to convert it into the fluid state, no change in the intensity of the scattered light was observed. This is shown by the results given in Table XIV.

Table XIV.

| Temperature. | Tyndall number in gel state. | Tyndall number in fluid state. |
|---|---|---|
| ° | | |
| 15 | 16·0 | 16·0 |
| 30 | 16·0 | 16·0 |
| 40 | 14·7 | 14·7 |
| 50 | 13·5 | 13·5 |

It was observed that, however long the gel was shaken, the Tyndall number did not change at all. The fluid obtained by this mechanical shaking was much more viscous and opalescent than the original sol. The above evidently shows that the micelles contained in the gel are bigger than those present in the original sol. If, according to McBain's view, the particles were identical, we should expect that this mechanical shaking would, to a great extent, break the bonds between the particles, and restore the original sol, with its small light-scattering capacity. But such is not actually the case.

Another view of the nature of gelatinisation which appears to have attracted much attention is that of Bradford,* who considers that gel-formation is a case of crystallisation. This theory seems to have been contradicted by the fact that X-ray analysis has failed to show any evidence of crystal formation in several gels, *e.g.*, gelatin.

Kraemer,† besides many other investigators, is of opinion that the formation of a gel is due to an incomplete precipitation of the disperse phase from a colloidal solution. If the gel formation be intimately associated with changes tending to precipitation, it should bring about an increase in the light-scattering capacity. This may be true in *several* cases, but the statement that gel-formation is associated with precipitation is *not always true*. This is shown by the fact that, when a gelatin sol (say, of 2 per cent. concentration) of $p$H 3·0 is kept at about 10° for a time, a gel is obtained, the light-scattering capacity of which is identical with that of the sol; and this remains unchanged for any length of time (several months). It follows from this that the micelles present in the gelatin sol undergo no change during gelation. The formation of the gel is here obviously due to the increase in the hydration of the colloidal micelles and their union.

Kraemer's view is further contradicted by the fact observed by the author that an agar sol of 0·5 per cent. concentration and $p$H 2·4 does not set to a gel on cooling and leaving it overnight at the room temperature (about 10° C.) while an agar sol of the same concentration, but of $p$H 5, sets to a gel when similarly treated. It has been observed that the final value of the Tyndall number was slightly greater in the former case than in the latter. Thus, though the tendency for precipitation was greater in the sol at $p$H 2·4 it did not set to a gel.

Further Kraemer has himself observed that over a narrow region at the isoelectric point at $p\text{H} = 4·95$, the gel-formation in a gelatin sol is very small (*cf.* 'Colloid Symp. Monograph,' IV, p. 113 (1926)), though the precipitation tendency, as revealed by the increase in Tyndall number, is a maximum at this point.

The above arguments show that the precipitation tendency is ***not always*** the main factor which is responsible for gel formation. It may be so in some cases. *The factor which is necessary and sufficient for gel formation is the union*

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* Alexander, 'Colloid Chemistry,' p. 751 (1926).

† 'J. Phys. Chem.,' vol. 29, p. 1523 (1925).

*of the micelles.* These may be monomolecular micelles (as in the case of metastyrol), colloid particles (as in cadmium gel prepared by Svedberg), or hydrated particles (as in the case of agar and gelatin gels). Further, the micelles which unite may be identical with those present in the original colloid, or they may grow to bigger dimensions before they unite. The latter is the case when the intermicellary liquid becomes supersaturated with respect to the molecularly dispersed substance. Any factor which favours the union of the particles helps the formation of a rigid gel, *e.g.*, (1) an increase in the number of colloidal micelles which brings them nearer together ; (2) an increase in the size of the micelles which has an effect similar to the one above. This explains why the more concentrated gels which also exhibit a greater light-scattering capacity are more rigid than the dilute ones. Even with gels of the same concentration a difference in *p*H may cause a difference in the strength of the gel, *e.g.*, a gelatin gel of *p*H 3·0 has a much lower light-scattering capacity than a gel of the same concentration but of *p*H 4·9, and is correspondingly weaker.

The observation of Kraemer that with a gelatin sol of *p*H 4·95 the gel formation is very small, though the Tyndall number is a maximum, can be explained as follows—It is known, from the measurements of Tyndall number, that the micelles which unite grow to very big dimensions. But the smaller the micelles are at the moment of binding the more uniform is the gel. Since, in the above case, the micelles rapidly grow to very large dimensions before they unite, cooling does not result in a uniform gel.

The gels exhibit such a great variety both in their manner of formation and their properties, that it is not possible to extend any single theory of gelatinisation to all the different classes of gels. The view that a gel is a solid framework of fibrils which become joined at their points of intersection is not always true but only in some cases. As has been shown above, certain gels (*e.g.*, gelatin gel at 3·0) are formed merely by the union of the hydrated micelles. In fact, the controversy in this field is mostly due to the fact that several investigators try to extend their particular theory to all gels.

In the previous sections a conception of gelatinisation has been developed which appears to be in complete harmony with all the observed facts. It is not claimed that this view can be extended to all kinds of gels ; but this holds in the case of agar gels, and others belonging to the same class.

## *Summary.*

(1) The effect of temperature on the intensity and depolarisation of the light scattered by agar sols and gels has been investigated; and a view regarding the nature of gelatinisation has been developed. Agar sols have been considered to be colloidal solutions having as the intermicellary liquid a molecularly dispersed solution of agar. Lowering the temperature of the sol to about 35° brings about a supersaturation of the molecularly dispersed agar, which therefore tends to precipitate. In the earlier stages it is probable that fresh colloidal particles are formed, but when these are sufficiently numerous further supersaturation is relieved by the agar condensing on the particles already present in the sol. Each of these micelles is surrounded by a hydration layer and the union of these hydrated micelles brings about the formation of a gel.

(2) A comparison of the light-scattering capacity of agar sols and gels at the same temperature, shows that gels are distinctly more opalescent; and hence the conclusion is drawn that the micelles present in gels are bigger than those in sols at the same temperature.

(3) The intensity of the scattered light (I) was found to increase with the concentration of the sols and gels. The regular increase of the ratio between I in the gel and sol states with concentration indicates that the micelles in the concentrated gels are bigger and more numerous than in the dilute ones.

(4) The intensity of the light scattered by agar sols increases continuously with time at and below 35° C.; the lower the temperature, the more rapid is the change.

The effect of sudden cooling of agar sols on the formation of gels, and their light-scattering capacity has been investigated. It was found that, in all cases, the formation of a gel was accompanied by a marked increase in the Tyndall number.

(5) The depolarisation factor ($\theta$) of the light scattered by agar sols and gels was also found to vary with temperature and concentration. With concentrated sols $\theta$ was found to increase steadily with decrease in temperature (below 35°), whereas in dilute sols (0·2 per cent.) $\theta$ decreases with temperature. With 0·5 per cent. sols $\theta$ was found to decrease at first, and, after reaching a minimum, to increase again. The light these results throw on the changes in size and shape of the particles in agar gels has been discussed.

(6) The existing theories of gel structure have been discussed, and the views of the author put forward. It has been shown that the micelles in gels are, in

several cases, bigger or more numerous than those in the sol. It has been emphasised that gel-formation is not always associated with the tendency for precipitation.

In conclusion, I desire to express my indebtedness to Prof. F. G. Donnan, C.B.E., F.R.S., for his very kind interest in this work, and the excellent facilities he has offered me for carrying out this research. My thanks are also due to the Government of Madras for the award of a scholarship.

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# *Structure of the Violet Bands of Silicon Nitride.*

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[Plate 5.]

The spectrum of the luminescence produced when silicon tetrachloride vapour reacts with glowing active nitrogen was first studied by Jevons.* He measured the heads of a group of bands occurring in the more refrangible part of the visible spectrum. These bands have single heads and are degraded towards the long wave-lengths. From the fact that a nitrogen-containing substance is deposited on the walls of the after-glow tube during the reaction, Jevons favoured the view that the bands are due to a nitride of silicon (SiN). This has been verified in a recent study of its spectrum by Mulliken.†

In this work, which was primarily concerned with the isotope effect, Jevons' measurements were revised and extended to include two faint companion systems of bands, due to isotopic molecules containing silicon of atomic weights 29 and 30. Further, Mulliken was able to establish spectroscopically the existence of the latter isotope, when the mass-spectrograph evidence was still inconclusive, and he included a description of a weaker system of bands distinct from the above, in that the heads are double and no frequency intervals occurred which agreed with those of the stronger system. Vibrational quantum numbers were assigned for the two systems, and the constants of the rotational structure of the stronger bands were determined by a procedure which was necessarily approximate, since spectrographs of moderate resolving power were used.

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* 'Roy. Soc. Proc.,' A, vol. 89, p. 187 (1913).

† 'Phys. Rev.,' vol. 26, p. 319 (1925).

It was therefore of interest to investigate the structure of the SiN bands by using an instrument of high resolving power. According to the recently developed systematic theory of the relation of band-spectrum structure to the electronic states of molecules,* the fine structure of the bands of any system is determined by the type of electronic transition involved. The stronger SiN system has been classified† among those resulting from a transition between two $^2S$ molecular terms. Other examples of this type are the band systems of AlO, $N_2^+$, $CO^+$ (negative Deslandres group), BO (β system), and the well-known violet CN system. Characteristic of these cases is the occurrence of single bands, each having almost equally intense P and R branches composed of narrow doublets. The separation of these doublets increases with the rotational quantum number. At the band origin a single gap occurs in the otherwise continuous series formed by the P and R branches. The appearance of the $^2S \rightarrow {}^2S$ SiN bands under moderate dispersion was entirely consistent with this structure, but only a few of the highest members of the line series were resolved, and neither the rotational doubling nor the absence of the single null-line could be established.

A further question which arises is whether, in the expression for the vibrational energy, the quantum numbers should take integral values, $n$, or whether $(n + 1/2)$ should be used, as is required in all cases by the quantum mechanics. An experimental decision between these alternatives could only be reached by the study of the vibrational isotope effect. Mulliken had shown‡ that for the BO spectrum, the half-integral numbering is definitely required, and one of the writers has recently obtained a quantitative measurement§ of the isotopic displacement of the (0, 0) bands|| of the two isotopic systems here involved.

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* 'Phys. Rev.,' vol. 28, p. 481 (1926), and succeeding papers of this series.

† 'Phys. Rev.,' vol. 26, p. 561 (1925).

‡ 'Phys. Rev.,' vol. 25, p. 259 (1925).

§ 'Proc. Nat. Acad. Sci.,' vol. 13, p. 496 (1927).

|| The notation used in the present communication conforms essentially with that of the Bulletin of the National Research Council, No. 57, 'Molecular Spectra in Gases.' An individual band is denoted by $(n', n'')$, where $n$ is the vibrational quantum number, and, as in the designation of other quantum numbers and constants, the single and double primes refer to the more and the less excited states, respectively.

Further evidence in the same direction has been obtained by Watson* from the MgH spectrum. In the case of SiN, however, Mulliken stated that his data seemed to favour the integral numbering, though the accuracy of his measurement did not justify a definite conclusion. Recently, Woldering† has asserted that a recalculation based on Mulliken's measurements gave evidence in favour of the quantum mechanics formulation. New data of higher precision was therefore required in order to reach a definite conclusion.

The present communication gives the results of an experimental investigation of the SiN spectrum, for which a large grating was employed. A number of the stronger violet bands due to the molecule containing the most abundant isotope, $Si^{28}N$, could be satisfactorily studied. They are completely resolved, except for several lines at the band head. A few heads belonging to the isotopic systems of $Si^{29}N$ and $Si^{30}N$ were of sufficient intensity for measurement, though their structure lines were not. No bands of the weaker double system were observed. Since active nitrogen spectra are particularly suited to the study of the vibrational energy terms and the effect of vibration on the rotational terms, it was of interest to measure the lines of all bands which appeared with any intensity. Because of the low temperature of the source, the number of lines in each branch of a band does not usually exceed 40, and on this account an accurate investigation of the higher terms in the rotational energy function has not been undertaken. Flame or arc spectra are more suited to this purpose, because a larger number of rotational terms can be evaluated in a given band by the combination principle. It has been found possible to calculate accurate values of the band origins, and to represent the observed combination differences within the limit of experimental error by using suitable constants in the theoretical formula. These band origins are then used to obtain expressions for the vibrational energy, for which the isotope effect requires the half-integral numbers of the quantum mechanics.

## *Experimental.*

The source of active nitrogen did not differ essentially from that used by Jevons. The conditions were so regulated as to obtain the greatest intensity of the purple glow. The nitrogen was purified before activation by being passed, first, through a tube 1 metre long containing moist phosphorus, and then through three similar tubes containing calcium chloride, soda lime and phosphorus pentoxide. A large-capacity pump kept the pressure at 30 mm. in the activating discharge, while the nitrogen passed through at about 20 litres per hour. The discharge took place between thick tungsten wires 12 cm. apart, and was produced by a high-potential transformer with condenser and spark-gap. The liquid silicon tetrachloride was separated from the after-glow tube by a narrow capillary, which, when adjusted to the proper size, allowed a constant flow of the vapour to pass. The volatile liquid $SiCl_4$ was used at the rate of about 1 c.c. per hour.

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* 'Nature,' vol. 117, p. 692 (1926).

† 'Naturw.,' vol. 15, p. 265 (1927).

The spectrograms were taken on the 21-foot Rowland concave grating at Harvard University, which gives a linear dispersion of 0·96 A. per millimetre in the second order. Two sets of plates were taken, with respective exposures of 3 and 9 hours. On the latter, doublets having a separation of 0·035 A. were clearly resolved in the second order spectrum. The wave-length measurements were made with reference to the international iron arc standards, as redetermined by Meggers, Kiess and Burns.* Table 1 contains the wave-numbers (*in vacuo*) of the lines of the 10 strongest bands. These include four in which the vibrational quantum number decreases by one during the emission ( (3, 2) to (6, 5) ), and six in which it is unchanged, (0, 0) to (5, 5). This table includes practically all the lines of any intensity which occur in this spectrum between the wave-lengths λλ 4000 and 4300 A. The wave-length (in air) of the band edge is given before the data for each band. In certain cases this is double, for a reason to be given later. The rotational quantum numbers, *m*, refer to the final state in emission, and are in accordance with the new numbering of the quantum mechanics. The intensity of the lines in each branch increases regularly from zero at the null-line to a maximum at $m = 14$ or 15, and falls off more slowly. Whenever a particular line departs appreciably from this regular intensity distribution, the fact is indicated in the table, by *s* if it is too strong, and *w* if too weak. The letter *d* signifies an exceptionally broad line, probably consisting of two or more unresolved components. A line marked *h* forms the head of the band. There exist several marked perturbations or irregularities in the spacing of the lines. The wave-numbers of perturbed lines are followed by *p*. The appearance of these phenomena, in addition to the general aspect of the spectrum, will be better understood by reference to the accompanying plate.

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* 'Bulletin Bureau of Standards,' vol. 19, p. 263 (1924).

Table I.

| *m*. | (0, 0) $\begin{cases}\lambda\,4116{\cdot}858\\ \lambda\,4117{\cdot}031\end{cases}$ | | (1, 1) $\begin{cases}\lambda\,4143{\cdot}130\\ \lambda\,4143{\cdot}251\end{cases}$ | |
|---|---|---|---|---|
| | R (*m*). | P (*m*). | R (*m*). | P (*m*). |
| 0 | | | 24,097·35 | |
| 1 | 24,239·37 | | 098·74 | 24,094·52 |
| 2 | 240·79 | 24,233·02 | 100·09 | 092·98 |
| 3 | 242·16 | 232·07 | 101·41 | 091·51 |
| 4 | 243·51 | 230·63 | 102·71 | 089·95 |
| 5 | 244·86 | 229·00 | 103·97 | 088·41 |
| 6 | 246·15 | 227·51 | 105·20 | 086·79 |
| 7 | 247·49 | 225·82 *d* | 106·38 | 085·16 |
| 8 | 248·73 | 224·24 *sd* | 107·57 | 083·48 |
| 9 | 249·95 | 222·61 *sd* | 108·73 | 081·82 |
| 10 | 251·22 | 220·98 *sd* | 109·85 | 080 11 |
| 11 | 252·46 *d* | 219·44 | 110·89 | 078·38 |
| 12 | 253·63 *d* | 217·73 | 111·92<br>112·21 *p* | 076·62 |
| 13 | 254·73<br>254·95 | 216·13 *sd* | 112·94<br>113·21 *d* | 074·77 |
| 14 | 255·80<br>256·05 | 214·35 | 113·93<br>114·18 | 073·23 *p*<br>072·90 |
| 15 | 256·93<br>257·21 | 212·73<br>212·44 | 114·93<br>115·18 | 071·38<br>071·05 |
| 16 | 258·08<br>258·29 | 210·95<br>210·75 | 115·86<br>116·13 | 069·46<br>069·18 |
| 17 | 259·15<br>259·40 | 209·11 *d* | 116·75<br>117·08 | 067·57<br>067·23 |
| 18 | 260·23<br>260·45 | 207·40 *d* | 117·63<br>117·86 *p* | 065·62<br>065·28 |
| 19 | 261·26<br>261·55 | 205·55 *d* | 118·35 *d*<br>118·81 | 063·68<br>063·30 |
| 20 | 262·25<br>262·56 | 203·73<br>203·52 | 119·30<br>119·61 | 061·52 *p*<br>061·34 |
| 21 | 263·21<br>263·61 | 201·71 *sd* | 120·10<br>120·45 | 059·69<br>059·30 |
| 22 | 264·23<br>264·61 | 199·99<br>199·57 *sd* | 120·82<br>121·15 | 057·63<br>057·24 |
| 23 | 265·22<br>265·57 | 198·18<br>197·85 | 121·51<br>121·91 | 055·57<br>055·14 |
| 24 | 266·14<br>266·50 | 196·31<br>195·94 | 122·22<br>122·65 | 053·43<br>053·01 |
| 25 | 267·03 *s*<br>267·42 *s* | 194·39<br>194·01 | 122·91<br>123·26 | 051·28<br>050·84 |
| 26 | 24,267·91 *s*<br>268·30 *s* | 24,192·67 *sd*<br>192·10 | 24,123·50<br>124·06 *d* | 24,049·11<br>048·65 |
| 27 | 268·77<br>269·22 | 190·23 *sd* | 124·06 *d*<br>124·62 | 046·90<br>046·49 |
| 28 | 269·63<br>270·03 | 188·36<br>187·77 *sd* | 124·62<br>125·16 | 044·71<br>044·26 |
| 29 | 270·47<br>270·83 | 186·40<br>186·08 | 125·16<br>125·69 | 042·47<br>041·98 |
| 30 | 271·23<br>271·63 | 184·41<br>183·95 | 125·69<br>126·14 | 040·12<br>039·65 |
| 31 | 271·97<br>272·41 | 182·35 *sd*<br>181·93 | 126·14<br>126·53 *d* | 037·89 *d*<br>037·30 |
| 32 | 272·68<br>273·13 | 180·17<br>179·62 *sd* | 126·53 *d*<br>127·13 | 035·45<br>034·91 |

Table I—(continued).

| *m*. | (0, 0) λ 4116·858, λ 4117·031 | | (1, 1) λ 4143·130, λ 4143·251 | |
|---|---|---|---|---|
| | R (*m*). | P (*m*). | R (*m*). | P (*m*). |
| 33 | 273·52<br>273·86 | 178·09<br>177·62 | 126·91<br>127·54 | |
| 34 | 274·18<br>274·66 | 176·04<br>175·51 | 127·13<br>127·90 | |
| 35 | 274·86<br>275·27 | 173·70 *sd* | 127·54<br>128·23 | |
| 36 | 275·51<br>275·82 | 171·73<br>171·16 | 127·90<br>128·50 | |
| 37 | 276·01<br>276·64 *d* | | 128·23<br>128·86 *h* | |
| 38 | 276·64 *d*<br>277·22 *d* | | | |
| 39 | 277·22 *d*<br>277·81 | | | |
| 40 | 277·81<br>278·27 | | | |
| 41 | 278·27<br>278·83 | | | |
| 42 | 278·83<br>279·32 | | | |

| *m*. | (2, 2) λ 4172·139 | | (3, 3) λ 4204·146 | |
|---|---|---|---|---|
| | R (*m*). | P (*m*). | R (*m*). | P (*m*). |
| 0 | 23,938·00 | | 23,760·82 | |
| 1 | 939·22 | 23,935·01 | 762·13 | 23,758·01 |
| 2 | 940·50 | 933·56 | 763·42 | 756·55 |
| 3 | 941·80 | 932·07 | 764·66 | 755·04 |
| 4 | 943·05 | 930·49 | 765·83 | 753·46 |
| 5 | 944·24 *d* | 928·94 *d* | 766·96 | 751·84 |
| 6 | 945·43 | 927·29 | 768·06 | 750·18 |
| 7 | 946·56 *d* | 925·63 | 769·08 | 748·47 |
| 8 | 947·63 | 923·92 | 770·06 | 746·70 |
| 9 | 948·69 | 922·17 | 771·00 | 744·89 |
| 10 | 949·69 *d* | 920·38 | 771·89 | 743·06 |
| 11 | 950·65 | 918·57 | 772·74 | 741·15 |
| 12 | 951·57 | 916·70 | 773·52 | 739·20 |
| 13 | 952·49 | 914·84 | 774·28 | 737·20 |
| 14 | 953·33 | 912·89 | 774·97 | 735·11 |
| 15 | 954·15 | 910·90 *d* | 775·59 | 733·04 |
| 16 | 954·92 *d* | 908·92 *d* | 776·18 *d* | 730·90 |
| 17 | 955·64 *d* | 906·95<br>906·74 | 776·72 *d* | 728·70 |
| 18 | 956·23<br>956·43 | 904·85<br>904·70 | 777·21 *d* | 726·44 |
| 19 | 956·87<br>957·10 | 902·87<br>902·55 | 777·67 | 724·13 |
| 20 | 957·46<br>957·70 | 900·58<br>900·34 | 778·09 | 721·80 |

Table I—(continued).

| *m*. | (2, 2) λ 4172·139 |  | (3, 3) λ 4204·146 |  |
|---|---|---|---|---|
|  | R (*m*). | P (*m*). | R (*m*). | P (*m*). |
| 21 | 958·01<br>958·26 | 898·39<br>898·13 | 778·48 *d* | 719·40 |
| 22 | 958·54<br>958·78 | 896·14<br>895·88 | 778·79 | 716·95 |
| 23 | 959·03<br>959·31 | 893·83<br>893·58 |  | 714·46 |
| 24 | 959·46<br>959·80 | 891·54<br>891·24 |  | 711·90 *d* |
| 25 | 959·80<br>960·16 | 889·17<br>888·84 |  | 709·32 *d* |
| 26 | 960·16<br>960·57 *d* | 886·78<br>886·44 |  | 706·76<br>706·59 |
| 27 |  | 884·33<br>884·01 |  | 704·06<br>703·89 |
| 28 |  | 881·90<br>881·49 |  | 701·36<br>701·14 |
| 29 |  | 879·41<br>878·93 |  | 698·54<br>698·38 |
| 30 |  | 23,876·75<br>876·27 |  | 23,695·72<br>695·48 |
| 31 |  | 874·56 *wp*<br>874·07 *sp* |  | 692·80<br>692·54 |
| 32 |  | 871·47<br>871·04 |  | 689·86<br>689·61 |
| 33 |  | 868·95<br>868·45 |  | 686·80<br>686·53 |
| 34 |  | 866·12<br>865·69 |  | 683·77<br>683·50 |
| 35 |  | 863·34<br>862·79 |  | 680·66<br>680·39 |
| 36 |  | 860·46<br>860·00 |  | 677·53<br>677·23 |
| 37 |  | 857·65<br>857·13 |  | 674·35<br>674·00 |
| 38 |  |  |  | 671·01<br>670·69 |

| *m*. | (4, 4) λ 4239·162 |  | (5, 5) λ 4277·084 |  |
|---|---|---|---|---|
|  | R (*m*). | P (*m*). | R (*m*). | P (*m*). |
| 0 | 23,567·79 |  |  |  |
| 1 | 569·23 | 23,565·24 | 23,362·78 | 23,358·77 |
| 2 | 570·55 | 563·78 | 363·93 | 357·37 |
| 3 | 571·71 | 562·23 | 365·06 | 355·73 |
| 4 | 572·85 | 560·68 | 366·13 | 354·12 |
| 5 | 573·89 | 559·03 | 367·11 | 352·44 |
| 6 | 574·91 | 557·31 | 368·08 | 350·73 |
| 7 | 575·87 | 555·56 | 368·94 | 348·94 |
| 8 | 576·73 | 553·76 | 369·71 | 347·03 |
| 9 | 577·53 | 551·87 | 370·45 | 345·08 |
| 10 | 578·32 | 549·95 | 371·08 | 343·11 |

Table I—(continued).

| *m.* | (4, 4) λ 4239·162 | | (5, 5) λ 4277·084 | |
|---|---|---|---|---|
| | R (*m*). | P (*m*). | R (*m*). | P (*m*). |
| 11 | 579·02 | 547·95 | 371·61 *d* | 341·02 |
| 12 | 579·70 *d* | 545·89 | 372·15 | 338·88 |
| 13 | 580·25 *dp* | 543·79 | 372·58 | 336·69 |
| 14 | 580·86 | 541·64 | 372·98 | 334·40 |
| 15 | 581·31 | 539·40 *dp* | 373·29 | 332·05 |
| 16 | 581·70 *d* | 537·17 | 373·58 | 329·62 |
| 17 | 582·04 *d* | 534·81 | 373·81 *sd* | 326·16 |
| 18 | 582·33 *p* | 532·41 | 373·87 *h* | 324·62 |
| 19 | 582·62 | 529·93 | | 321·98 |
| 20 | 582·88 *sd* | 527·72 *wp*<br>527·35 *p*<br>526·88 *wp* | | 319·29 |
| 21 | 582·95 *h* | 524·82 | 373·81 *sd* | 316·55 |
| 22 | | 522·22 *dp* | 373·58 *s* | 313·72 |
| 23 | | 519·48 | 373·29 *s* | 310·81 *d* |
| 24 | | 516·73 | 372·98 *s* | 307·85 |
| 25 | | 513·90 | 372·58 *s* | 304·82 |
| 26 | | 511·02 | 372·15 *s* | 301·68 |
| 27 | | 508·08 | 371·61 *sd* | 298·51 |
| 28 | | 505·06 | 370·88 | 295·29 |
| 29 | | 502·01 | 370·13 | 291·94 |
| 30 | | 498·87 | 369·38 | 288·50 |
| 31 | | 495·71 | 368·54 | 285·09 |
| 32 | | 492·43 | 367·65 | 281·48 |
| 33 | | 489·14 *d* | 366·58 *dp* | 277·94 *dp* |
| 34 | | 485·76 *d* | 365·54 *d* | 274·26 |
| 35 | | 482·49<br>482·28 | 364·50 *d* | 270·40 *d* |
| 36 | | 478·95<br>478·77 | 363·16 *d* | 266·66 *d* |
| 37 | | 475·35<br>475·08 | | |
| 38 | | 471·73<br>471·48 | | |
| 39 | | 468·11<br>467·86 | | |

| *m.* | (3, 2) λ 4016·829 | | (4, 3) λ 4050·786 | |
|---|---|---|---|---|
| | R (*m*). | P (*m*). | R (*m*). | P (*m*). |
| 0 | | | 24,667·34 | |
| 1 | 24,874·47 | | 668·52 | 24,664·44 |
| 2 | 875·71 | 24,868·85 | 669·73 | 662·91 |
| 3 | 876·90 | 867·20 | 670·84 | 661·37 |
| 4 | 878·06 | 865·68 | 671·96 | 659·71 |
| 5 | 879·11 | 863·96 | 672·91 | 658·01 |
| 6 | 880·15 | 862·28 | 673·87 | 656·26 |
| 7 | 881·13 *d* | 860·52 | 674·75 | 654·41 |
| 8 | 882·02 | 858·65 | 675·52 | 652·51 |
| 9 | 882·85 *d* | 856·75 | 676·25 | 650·54 |

Table I—(continued).

| *m*. | (3, 2) λ 4016·829 |  | (4, 3) λ 4050·786 |  |
|---|---|---|---|---|
|  | R (*m*). | P (*m*). | R (*m*). | P (*m*). |
| 10 | 883·62 | 854·74 | 676·90 | 648·51 |
| 11 | 884·33 | 852·77 | 677·46 | 646·38 |
| 12 | 884·96 | 850·66 | 677·93 *p*<br>678·15 *p* | 644·22 |
| 13 | 885·54 | 848·49 | 678·35 *p*<br>678·55 *p* | 641·93 |
| 14 | 886·08 | 846·27 | 678·88 | 639·64 *dp* |
| 15 | 886·56 | 844·05 | 679·18 | 637·21 *dp* |
| 16 | 886·96 | 841·69 |  | 634·78 |
| 17 | 887·28 | 839·31 |  | 632·27 |
| 18 | 887·59 | 836·86 *d* |  | 629·65 |
| 19 |  | 834·37 *d* |  | 626·96 |
| 20 |  | 831·91<br>831·64 |  | 624·50 *wp*<br>624·13 *p*<br>623·74 *wp* |
| 21 |  | 829·31<br>829·06 |  | 621·41 *d* |
| 22 |  | 826·61<br>826·35 |  | 618·55 *dp* |
| 23 |  | 823·85<br>823·60 | 679·18 *s*<br>678·88 *s* | 615·57 |
| 24 |  | 821·12<br>820·78 | 678·88 *s*<br>678·55 *s* | 612·54 |
| 25 |  | 818·16<br>817·88 | 678·35 *s*<br>678·15 *s* | 609·46 |
| 26 |  | 815·25<br>814·95 | 677·93 *s*<br>677·46 *s* | 606·26 |
| 27 |  | 812·21<br>811·92 | 677·46 *s*<br>676·90 *s* | 603·00 *d* |
| 28 |  | 809·21<br>808·91 | 676·41 *d* | 599·73 *d* |
| 29 |  | 806·03<br>805·69 | 675·78 *d* | 596·45<br>596·21 |
| 30 |  | 802·94<br>802·52 | 675·07 *d* | 592·99<br>592·74 |
| 31 |  | 799·68<br>799·29 | 674·26<br>673·87 *s* | 589·41<br>589·22 |
| 32 |  | 796·31<br>795·94 | 673·30<br>672·91 *s* | 585·83<br>585·55 |
| 33 |  |  | 672·35<br>671·96 *s* | 582·12<br>581·89 |
| 34 |  |  | 671·29<br>670·84 *s* | 578·36<br>578·13 |
| 35 |  |  | 670·15<br>669·73 *s* | 574·64<br>574·30 |
| 36 |  |  | 668·94<br>668·52 *s* | 570·72<br>570·44 |
| 37 |  |  | 667·34 *sd* | 566·74<br>566·44 |
| 38 |  |  | 666·08 |  |

Table I—(continued).

| m. | (5, 4) λ 4087·471 | | (6, 5) λ 4126·668 | |
|---|---|---|---|---|
| | R (*m*). | P (*m*). | R (*m*). | P (*m*). |
| 0 | 24,447·78 | | | |
| 1 | 448·98 | 24,444·93 | | |
| 2 | 449·97 | 443·36 *d* | 24,218·72 | |
| 3 | 451·10 | 441·74 | 219·86 | |
| 4 | 452·08 | 440·08 | 220·90 *s* | 24,209·11 *s* |
| 5 | 453·04 | 438·34 *d* | 221·74 | 207·40 *s* |
| 6 | 453·90 | 436·56 | 222·62 *s* | 205·55 *s* |
| 7 | 454·67 | 434·68 | 223·20 | 203·62 *s* |
| 8 | 455·39 | 432·72 | 223·95 | 201·60 *sd* |
| 9 | 455·96 | 430·68 | 224·40 *s* | 199·57 *s* |
| 10 | 456·52 | 428·55 | 224·82 | 197·30 |
| 11 | 457·08 *d* | 426·37 | 225·23 | 195·06 |
| 12 | 457·39 | 424·07 | 225·69 *sd* | 192·68 *s* |
| 13 | 457·73 | 421·72 | 225·82 *h* | 190·22 *sd* |
| 14 | 458·03 *sd* | 419·30 | | 187·67 *sd* |
| 15 | 458·13 *h* | 416·78 | | 185·07 *d* |
| 16 | | 414·17 | | 182·35 *d* |
| 17 | | 24,411·49 | | 24,179·69<br>179·57 |
| 18 | 24,458·03 *sd* | 408·75 | | 176·77<br>176·59 |
| 19 | 457·73 *s* | 405·91 | | 173·80<br>173·53 |
| 20 | 457·39 *s* | 403·01 | | 170·76<br>170·50 |
| 21 | 457·08 *sd* | 399·99 | | 167·61<br>167·31 |
| 22 | 456·69 | 396·94 | | 164·39<br>164·10 |
| 23 | 456·21 | 393·78 | | 161·00<br>160·70 |
| 24 | 455·59 | 390·52 | | 157·57<br>157·28 |
| 25 | 454·95 | 387·20 | | 154·07<br>153·71 |
| 26 | 454·22 | 383·81 | | 150·48<br>150·14 |
| 27 | 453·34 | 380·30 | | 146·75<br>146·45 |
| 28 | 452·38 | 376·74 | | 143·01<br>142·57 |
| 29 | 451·39 | 373·12 | | 139·09<br>138·74 |
| 30 | 450·25 | 369·35 | | 135·16<br>134·77 |
| 31 | 448·98 | 365·51 | | 131·10<br>130·63 |
| 32 | 447·78 | 361·63 | | |
| 33 | 446·39 | 357·59 *d* | | |
| 34 | 444·93 | 353·58 | | |
| 35 | 443·36 *d* | 349·40 | | |
| 36 | 441·74 | 345·19 *d* | | |
| 37 | 440·08 | 340·81 | | |
| 38 | 438·18 | 336·43 | | |
| 39 | 436·23 | 331·88 | | |
| 40 | 434·19 | 327·28 *d* | | |
| 41 | | 322·64 *d* | | |
| 42 | | 317·81 *d* | | |

### *The Rotational Structure.*

It is clear that the line structure of the bands is in accord with that to be expected for a $^2S \rightarrow {}^2S$ system. One line is missing at the origin, and the members of each branch are resolved into narrow doublets at higher rotational quantum numbers. The components of these doublets are in general of equal intensity. Their separation in a given band increases nearly linearly with $m$, until its highest values are reached. There is a general tendency towards the decrease of the separations with increasing vibrational quantum number. In the (0, 0) and (1, 1) bands the doubling is greatest, and the head is relatively far from the origin, with the result that a very close double head is formed. The (6, 5) band is exceptional in that it shows an unexpectedly large doubling. The doublet separations are equal for the (2, 2) and (3, 2) bands, as also for the (3, 3) and (4, 3) bands.

In general, doublets of this type arise from transitions between double initial terms and double final terms, the allowed transitions taking place in such a way that the observed doublet separations represent the difference between the term doubling in the initial and that in the final state. The only inference, therefore, which can be drawn from the above-mentioned equalities is that whatever variation takes place in the magnitude of this term doubling between the states $n = 2$, 3 and 4 must be in the final electronic configuration. It is not possible to determine its absolute value for any given state. From the observed doublet separations it may be definitely stated, however, that the term doubling does not bear any simple relation to the vibrational quantum number.

Several interesting perturbations occur, as in the analogous violet CN bands. These usually take the form of an exceptionally wide or an exceptionally narrow doublet, and faint satellite lines are often visible in the immediate neighbourhood of the perturbed line. These irregularities are connected in every case with the initial electronic state, as is shown by the fact that the lines R $(m - 1)$ and P $(m + 1)$, and also bands of the same $n'$, show similar perturbations. In the (1, 1) band a remarkable phenomenon occurs. Starting from the null-line, the lines broaden out gradually in each branch, indicating an unresolved doubling of the usual type. However, the lines having $m' = 11$ are again narrower, and those having $m' = 12$ are very sharp. At $m' = 13$ wide doublets begin, the high-frequency component of each doublet lying in the position to be expected from extrapolation of the preceding series. The separation of these doublets decreases slightly to $m' = 15$, increases again to $m' = 18$, and the lines $m' = 19$ are extremely narrow doublets with faint side components. $m' = 20$ again shows a relatively large doubling, which increases regularly for the remaining members as far as they can be traced. This peculiar behaviour somewhat resembles that found[*] in the (11, 11) band (one of the "tail" bands) of the violet CN system. It suggests an intimate connection between the perturbations and the rotational doubling, which will be of importance when a theory is developed to explain these features.

According to the quantum mechanics, the rotational energy terms in wave-number units are given by the expression

$$F(m) = Bm(m+1) + D[m(m+1)]^2 + \ldots . \qquad (1)$$

For $^2S$ states $m = j - \rho$, where $\rho$ is the resultant electronic angular momentum in units $h/2\pi$ perpendicular to the nuclear axis. It is usually almost exactly equal to $\pm 1/2$, since it corresponds essentially to the spin angular momentum of a single electron, which has two possible orientations, parallel and anti-parallel, to the nuclear angular momentum, $m$. Since $j$ measures the total angular momentum of the molecule, it is the true quantum number, and takes values which are accurately half-integral. In the present case, however, it may be assumed that $\rho = \pm 1/2$ exactly, and hence that the $m$'s are true integers, for an investigation of the empirical form of the combination differences to be discussed below showed that this is probably true within experimental error. Denoting by $\nu_0$ the band origin, *i.e.*, the point at which the rotational energy vanishes in both initial and final states, the wave-numbers of the lines in a band may be represented by

$$\left.\begin{aligned} R(m) &= \nu_0 + F'(m+1) - F''(m) && \text{(A)} \\ &= \nu_0 - \tfrac{1}{4}C + B' + 2B'(m+\tfrac{1}{2}) + C(m+\tfrac{1}{2})^2 + 4D'(m+\tfrac{1}{2})^3 \\ &\qquad + E(m+\tfrac{1}{2})^4 + \ldots && \text{(B)} \\ P(m) &= \nu_0 + F'(m-1) - F''(m) && \text{(A)} \\ &= \nu_0 - \tfrac{1}{4}C + B' - 2B'(m+\tfrac{1}{2}) + C(m+\tfrac{1}{2})^2 - 4D'(m+\tfrac{1}{2})^3 \\ &\qquad + E(m+\tfrac{1}{2})^4 + \ldots, && \text{(B)} \end{aligned}\right\} \qquad (2)$$

in which $C = B' - B''$ and $E = D' - D''$. By the application of the combination principle to the lines of a band, the rotational terms cannot be found directly, but only certain differences between neighbouring terms. In the present case, the following combination differences can be evaluated :—

$$\begin{aligned} \Delta_2F'(m) &= R(m) - P(m) = F'(m+1) - F''(m-1) \\ &= 4B'(m'+\tfrac{1}{2}) + 8D'(m'+\tfrac{1}{2})^3 + \ \ldots \qquad (3\text{A}) \\ \Delta_2F''(m) &= R(m-1) - P(m+1) = F''(m+1) - F''(m-1) \\ &= 4B''(m''+\tfrac{1}{2}) + 8D''(m''+\tfrac{1}{2})^3 + \ \ldots . \qquad (3\text{B}) \end{aligned}$$

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[*] 'Phys. Rev.,' vol. 31, p. 539 (1928).

The differences (3A) should be identical for all bands of the same $n'$, and (3B) for those of the same $n''$. With the assignment of rotational quantum numbers given in Table I, this requirement is fulfilled within the experimental error of measurement, which on the average does not appear to exceed 0·02 cm.$^{-1}$. In taking these combination differences, the mean wave-number of the doublet components was used when the line was double. Fig. 1 shows the accuracy with which the combination principle is followed in all cases where it could be tested. The figure gives the residuals of the observed values of $\Delta_2F$ from those calculated by the theoretical equations (3). Circles and crosses refer to data from different bands, as shown at the right of each set. Certain cases where there appears to be a definite trend in the residuals, for instance for the (5, 5) band between $m = 22$ and 29, are the result of the near coincidence of two series of lines (in this case two portions of the R branch near the head) which form unresolved doublets, but were measured as single lines. The maximum error which could be introduced in this way should be one-half the limit of resolution, or about 0·1 cm.$^{-1}$.

Fig. 1 also shows how well the observed combination differences are represented by equations (3). The coefficients B and D were determined as follows: For $n = 0$, D may be calculated by Kratzer's theoretical formula*

$$D_0 = -\frac{4B_0^3}{\omega_0^2}. \tag{4}$$

The vibration frequency for infinitesimal amplitudes, $\omega_0$, was known from Mulliken's work. Sufficiently accurate preliminary values of $B_0$ were found from the combination differences of the (0, 0) band by a graphical method. For the other vibrational states

$$D = D_0 + \beta n, \tag{5}$$

in which $\beta$ can also be calculated by a theoretical relation† originally derived by Kemble. Having these values of D, which presumably are of considerable accuracy, one computes the term $8D(m+\frac{1}{2})^3$ and subtracts it in each case from the observed $\Delta_2F$'s. The linear least squares solution of the resulting quantities, assuming the constant term to be zero, then gives a very good value of B. The constants determined in this manner are summarised in Table II. The equations which represent them are :—

$$\left.\begin{aligned} B' &= 0\cdot7235 - 0\cdot01037\,(n'+\tfrac{1}{2}) \\ B'' &= 0\cdot7310 - 0\cdot00567\,(n''+\tfrac{1}{2}) \end{aligned}\right\} \tag{6}$$

$$\left.\begin{aligned} D' &= -\,[1\cdot400 + 0\cdot0788\,(n'+\tfrac{1}{2})]\,10^{-6} \\ D'' &= -\,[1\cdot182 + 0\cdot0010\,(n''+\tfrac{1}{2})]\,10^{-6} \end{aligned}\right\}. \tag{7}$$

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* 'Ann. Physik,' vol. 71, p. 72 (1923).

† 'Phys. Rev.,' vol. 29, p. 59 (1927).

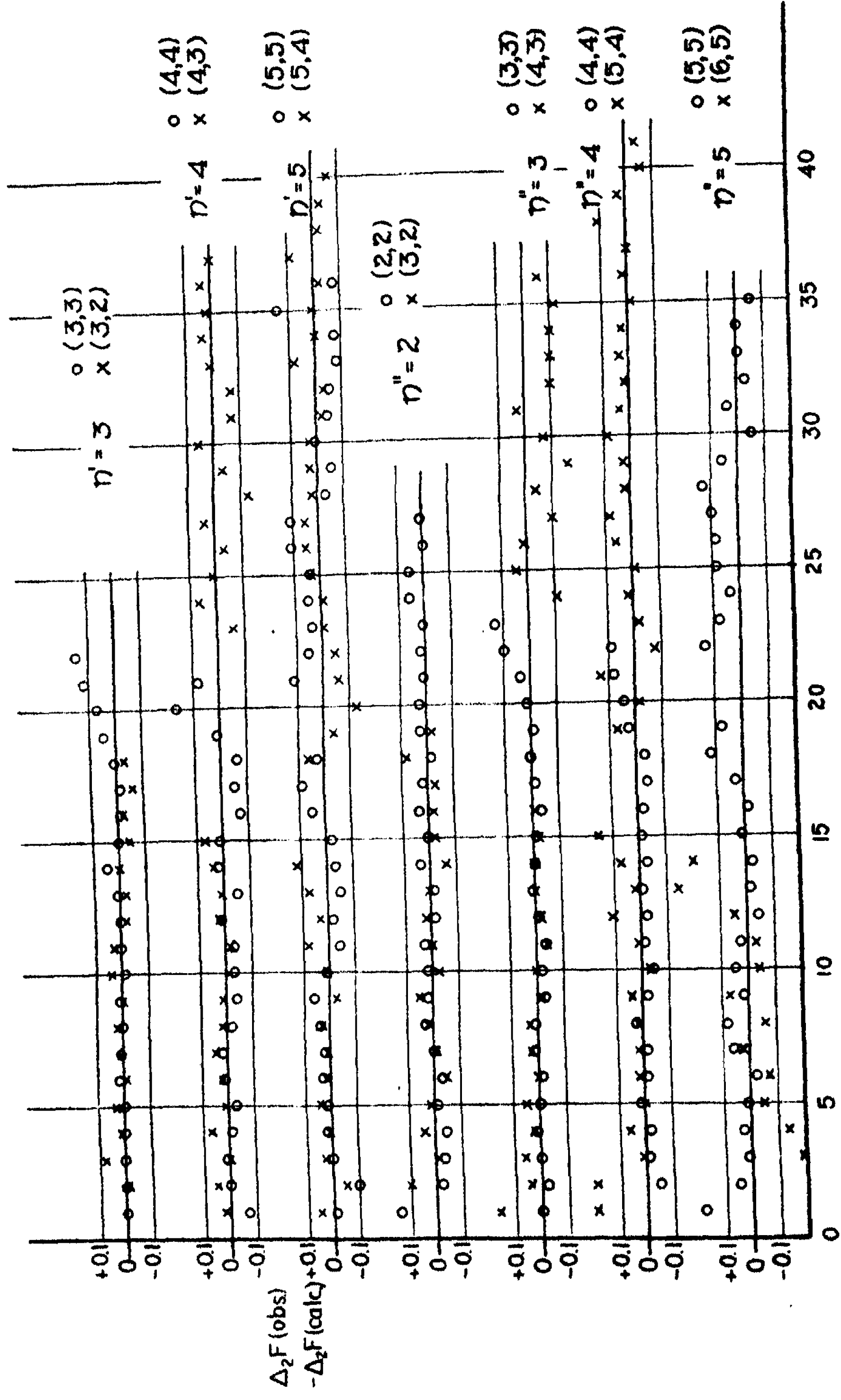
v' = 3
o (3,3)
x (3,2)
v' = 4
o (4,4)
x (4,3)
v' = 5
o (5,5)
x (5,4)
v'' = 2
o (2,2)
x (3,2)
v'' = 3
o (3,3)
x (4,3)
v'' = 4
o (4,4)
x (5,4)
v'' = 5
o (5,5)
x (6,5)
+0.1
0
-0.1
Δ₂F (obs) - Δ₂F (calc)
m →
0
5
10
15
20
25
30
35
40

FIG. 1.

## Table II.

| $v''$ | 0. | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | |
|---|---|---|---|---|---|---|---|---|---|---|
| $v'$<br>0 | 0·7181 (1)<br>0·7280 (2)<br>24,236·53 (3)<br>24,236·53 (4) | | | | | | | | | 0·7181 (9)<br>0·7183 (10)<br>−1·439 (11)<br>×10⁻⁶ |
| 1 | | 0·7081 (1)<br>0·7226 (2)<br>24,095·93 (3)<br>24,095·94 (4) | | | | | | | | 0·7081 (9)<br>0·7079 (10)<br>−1·518 (11) |
| 2 | | 3985·80 (5)<br>19·81 (6)<br>25,062·2 (7)<br>25,061·90 (4) | 0·6979 (1)<br>0·7171 (2)<br>23,936·47 (3)<br>23,936·45 (4) | | | | | | | 0·6979 (9)<br>0·6976 (10)<br>−1·596 (11) |
| 3 | | | 0·6868 (1)<br>0·7165 (2)<br>24,871·76 (3)<br>24,871·77 (4) | 0·6873 (1)<br>0·7114 (2)<br>23,759·44 (3)<br>23,759·45 (4) | 4406·90 (5)<br>25·21 (6)<br>22,660·1 (7)<br>22,660·25 (4) | | | | | 935·29 (8)<br>0·6871 (9)<br>0·6872 (10)<br>−1·675 (11) |
| 4 | | | | 0·6770 (1)<br>0·7115 (2)<br>24,665·85 (3)<br>24,665·85 (4) | 0·6762 (1)<br>0·7053 (2)<br>23,566·65 (3)<br>23,566·65 (4) | 4443·13 (5)<br>19·98 (6)<br>22,480·4 (7)<br>22,480·58 (4) | 4664·32 (5)<br>25·36 (6)<br>21,408·0 (7)<br>21,407·52 (4) | | | 906·41 (8)<br>0·6765 (9)<br>0·6768 (10)<br>−1·754 (11) |
| 5 | | | | | 0·6664 (1)<br>0·7056 (2)<br>24,446·21 (3)<br>24,446·21 (4) | 0·6662 (1)<br>0·6997 (2)<br>23,360·13 (3)<br>23,360·13 (4) | 4482·36 (5)<br>16·38 (6)<br>22,287·1 (7)<br>22,287·17 (4) | 4705·13 (5)<br>20·08 (6)<br>21,227·4 (7)<br>21,227·33 (4) | | 879·56 (8)<br>0·6663 (9)<br>0·6664 (10)<br>−1·833 (11) |
| 6 | | | | | 3949·78 (5)<br>9·33 (6)<br>25,301·4 (7)<br>25,301·32 (4) | 0·6563 (1)<br>0·6996 (2)<br>24,215·23 (3)<br>24,215·23 (4) | 4317·65 (5)<br>11·99 (6)<br>23,142·3 (7)<br>23,142·28 (4) | 4524·32 (5)<br>13·75 (6)<br>22,082·9 (7)<br>22,082·44 (4) | 4748·65 (5)<br>16·38 (6)<br>21,036·4 (7)<br>21,035·72 (4) | 855·10 (8)<br>0·6563 (9)<br>0·6561 (10)<br>−1·912 (11) |
| 7 | | | | | | 3989·88 (5)<br>8·32 (6)<br>25,048·0 (7)<br>25,048·64 (4) | 4168·23 (5)<br>9·21 (6)<br>23,975·1 (7)<br>23,975·68 (4) | 4360·71 (5)<br>10·32 (6)<br>22,915·3 (7)<br>22,915·84 (4) | | 0·6457 (10)<br>−1·990 (11) |
| 8 | | | | | | | 4031·99 (5)<br>7·48 (6)<br>24,787·2 (7)<br>24,790·47 (4) | 4211·89 (5)<br>8·20 (6)<br>23,727·5 (7)<br>23,730·63 (4) | | 0·6353 (10)<br>−2·069 (11) |
| 9 | | | | | | | | 4076·69 (5)<br>6·76 (6)<br>24,516·1 (7)<br>24,530·21 (4) | | 0·6250 (10)<br>−2·148 (11) |
| 10 | | | | 1112·32 (8) | 1099·20 (8) | 1086·08 (8) | | | 4119·45 (5)<br>6·14 (6)<br>24,262·1 (7)<br>24,271·65 (4) | 0·6146 (10)<br>−2·227 (11) |
| | 0·7280 (9)<br>0·7282 (10)<br>−1·182 (11)<br>×10⁻⁶ | 0·7226 (9)<br>0·7225 (10)<br>−1·183 (11) | 0·7169 (9)<br>0·7168 (10)<br>−1·184 (11) | 0·7114 (9)<br>0·7112 (10)<br>−1·185 (11) | 0·7055 (9)<br>0·7056 (10)<br>−1·186 (11) | 0·6997 (9)<br>0·6998 (10)<br>−1·187 (11) | 0·6942 (10)<br>−1·188 (11) | 0·6885 (10)<br>−1·189 (11) | 0·6828 (10)<br>−1·190 (11) | |

(1) Empirical $B'$.
(2) ,, $B''$.
(3) ,, $\nu_0$.
(4) $\nu_0$ from equation (9).
(5) Measured $\lambda_{head}$.
(6) Calculated $\nu_{head} - \nu_0$.
(7) $\nu_0$ calculated from $\lambda_{head}$.
(8) Vibrational term difference.
(9) Weighted mean B.
(10) B from equation (6).
(11) D from equation (7).

From the constant terms of equations (6), the moment of inertia of the non-vibrating molecule is found to be $38{\cdot}29 \times 10^{-40}$ and $37{\cdot}89 \times 10^{-40}$ gr. cm.$^2$ in the initial and final states respectively. Assuming this molecule to be $Si^{28}N$, the corresponding internuclear distances are $1{\cdot}576 \times 10^{-8}$ and $1{\cdot}568 \times 10^{-8}$ cm.

### *The Vibrational Structure.*

The vibrational energy of a diatomic molecule may be written

$$E_n = (n + \tfrac{1}{2})\, h\omega_0 \,[1 - x\,(n + \tfrac{1}{2}) + y\,(n + \tfrac{1}{2})^2 + z\,(n + \tfrac{1}{2})^3 + \ldots], \tag{8}$$

where $n = 0, 1, 2, \ldots$. The quantum mechanics justification for using $(n + \frac{1}{2})$ in powers higher than the first seems to be uncertain, although this form has been given by Fues.* Experimental evidence in its favour has been obtained in the present work, and will be presented below in connection with the isotope effect. It was necessary for the study of the vibrational terms to obtain first accurate values for the origins of all bands measured. This calculation was made by applying equations (2A) to several lines of each branch, for which the rotational terms were found by equations (1). The empirical $\nu_0$, which is actually identical with the wave-number of the null-line, is given in Table II for each of the 10 bands whose fine-structure was measured. Using these values, the following equation was obtained by the method of least squares:

$$\begin{aligned}\nu_0 = {} & 24{,}299{\cdot}40 + 1031{\cdot}007\,(n' + \tfrac{1}{2}) - 16{\cdot}7428\,(n' + \tfrac{1}{2})^2 \\ & + 0{\cdot}11722\,(n' + \tfrac{1}{2})^3 + 0{\cdot}014167\,(n' + \tfrac{1}{2})^4 - 1151{\cdot}680\,(n'' + \tfrac{1}{2}) \\ & + 6{\cdot}5600\,(n'' + \tfrac{1}{2})^2.\end{aligned} \tag{9}$$

The origins of other fainter bands of the system, of which the heads only had been measured, were next calculated from this expression and compared with the $\nu_0$ values obtained by subtracting the theoretical wave-number difference between heads and origins from the observed wave-numbers of the heads. The results of this comparison, which will also be found in Table II, are on the whole satisfactory, although there is an unaccountably large deviation at the higher values of $n'$. The correction from head to origin was obtained by substituting the numerical value of $B'/C$ in the equation (2B) relating to the R branch.

### *The Isotope Effect.*

The above analysis concerns only the bands of the system due to the predominating isotopic molecule, $Si^{28}N$. Of the systems due to $Si^{29}N$ and $Si^{30}N$, the heads of the (2, 2), (3, 3), (4, 4), (5, 5) and (6, 6) bands were visible on the plates, although the first and last of these were too faint to be accurately measured. In order to test the theoretical relations for the isotope effect derived by Mulliken,* the isotopic displacements of the heads were calculated by his equations and compared with those observed. Each displacement may be divided into two parts, the vibrational and rotational isotope effects. The vibrational effect (displacement of the origins) was obtained by setting up the vibrational equations for the $\mathrm{Si^{29}N}$ and $\mathrm{Si^{30}N}$ systems, corresponding to equation (9). To do this, we multiply each coefficient of equation (9) by the appropriate power of $\rho$, a quantity which depends only on the masses of the two isotopes and on that of the non-isotopic atom. The displacement due to the rotational effect, which is to be added to the above, can be obtained when $B'$ and $C$ are known in all three systems, for the distance in wave-number units from the head to the origin of any band is, approximately,

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* 'Ann. Physik,' vol. 80, p. 367 (1926).

$$\nu_{\text{head}} - \nu_0 = B' - B'^2/C. \tag{10}$$

From the constants in equation $B = B_0 - \alpha\,(n + \tfrac{1}{2})$, which have been found for $\mathrm{Si^{28}N}$ (*cf.* equations (6)), those for the other two systems are obtained by multiplying $B_0$ by $\rho^2$, and $\alpha$ by $\rho^3$. The results of this calculation are summarized in Table III.

Table III.

| | Bands. | Isotopic displacements. | | Theoretical. | | Observed $\Delta\nu_{\text{head}}$. |
|---|---|---|---|---|---|---|
| | | Vibrational. | Rotational. | $\Delta\nu_{\text{head}}$ $(n + \frac{1}{2})$. | $\Delta\nu_{\text{head}}$ $(n)$. | |
| | (1) | (2) | (3) | (4) | (5) | (6) |
| $\mathrm{Si^{29}N} - \mathrm{Si^{28}N}$ | (2, 2) | 2·42 cm.$^{-1}$ | −0·23 | 2·19 | 1·71 | 2·09 |
| | (3, 3) | 3·73 | −0·16 | 3·57 | 3·04 | 3·49 |
| | (4, 4) | 5·18 | −0·12 | 5·06 | 4·49 | 5·06 |
| | (5, 5) | 6·73 | −0·10 | 6·63 | 6·03 | 6·67 |
| $\mathrm{Si^{30}N} - \mathrm{Si^{28}N}$ | (2, 2) | 4·70 | −0·44 | 4·26 | 3·32 | 3·98 |
| | (3, 3) | 7·23 | −0·32 | 6·91 | 5·88 | 6·98 |
| | (4, 4) | 10·04 | −0·25 | 9·79 | 8·68 | 9·78 |
| | (5, 5) | 13·05 | −0·20 | 12·85 | 11·66 | 12·93 |

Column (4) contains the net displacements calculated by the above procedure. They are seen to be in excellent agreement with the observed values of column (6). In column (5) are tabulated the theoretical separations of the heads calculated on the assumption that the vibrational quantum numbers are integral, without introducing the half-unit required by the quantum mechanics. The results evidently show that the older formulation is wrong. Fig. 2 illustrates this graphically. The solid and broken lines give, respectively, the displacements predicted by the new and old quantum theories, while the circles are observed values. The accuracy with which these data support the formulation of the new quantum mechanics may be most concisely expressed in the

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* 'Phys. Rev.,' vol. 25, p. 119 (1925).

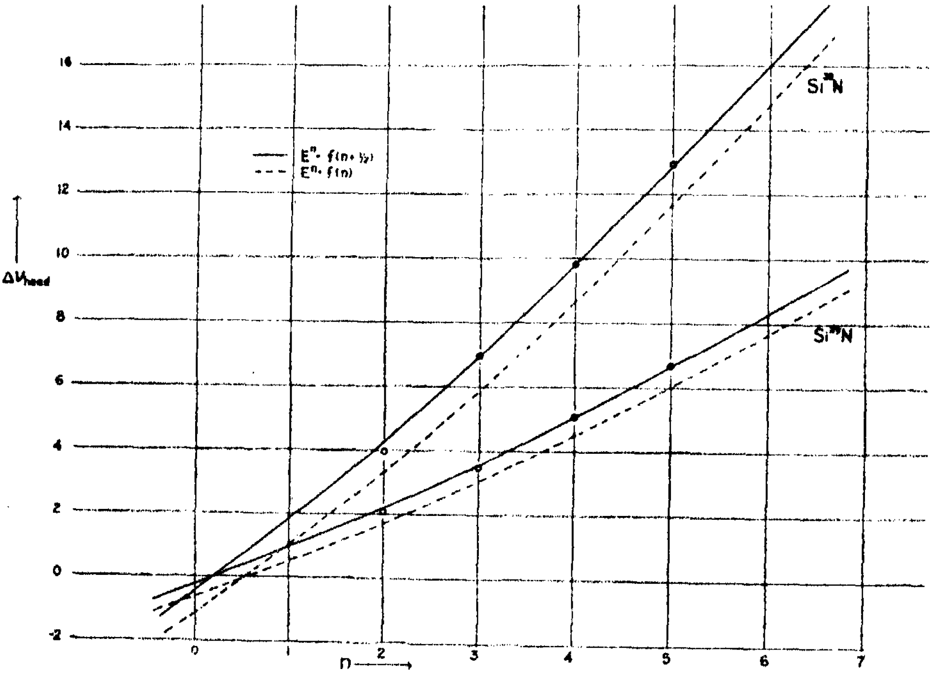


Fig. 2.

## DESCRIPTION OF PLATE 5.

(1), (2) and (3).—Strongest bands of the silicon nitride spectrum. Iron arc comparison spectrum.

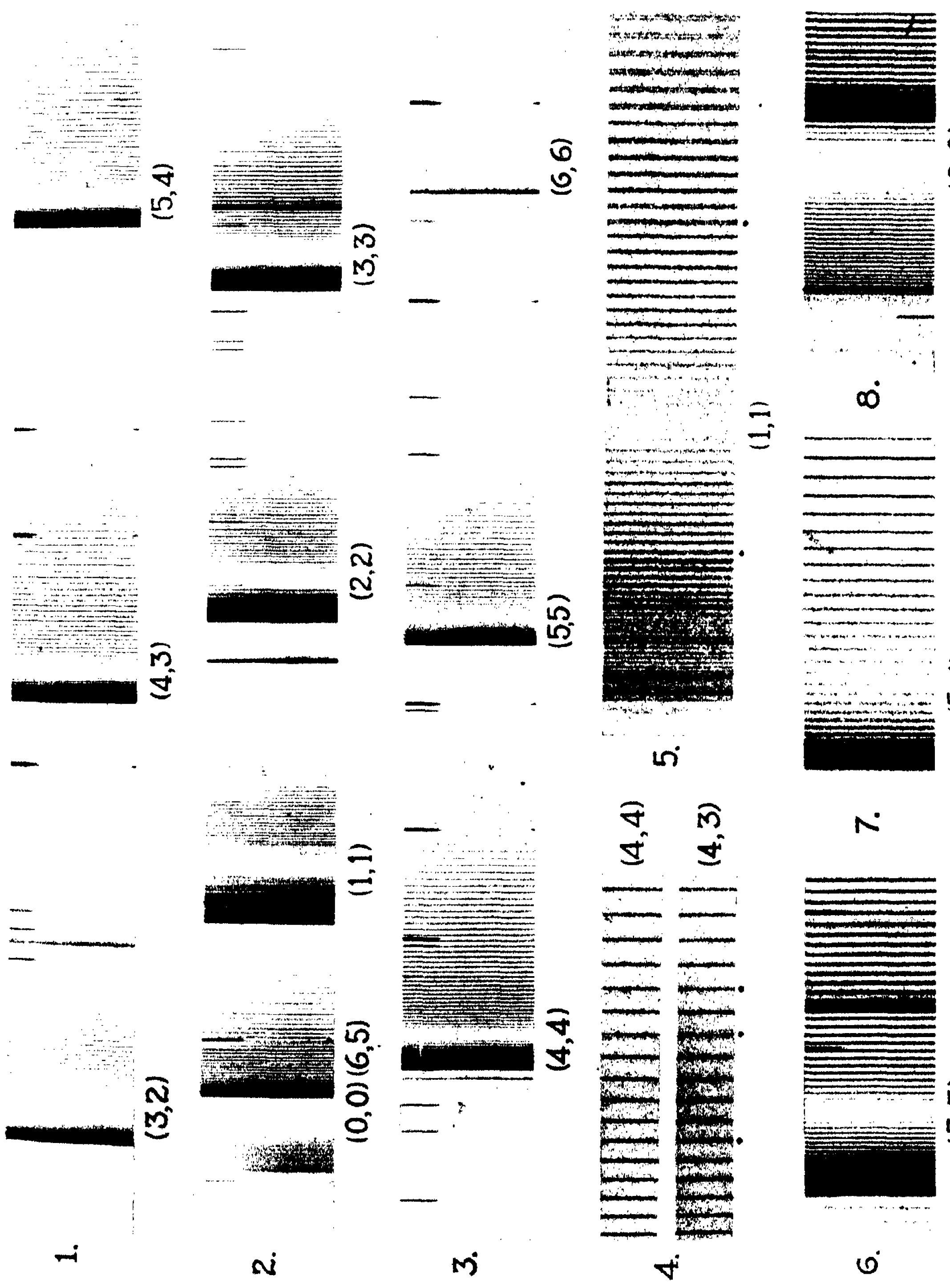
(4).—Portion of the P branches of the (4, 4) and (4, 3) bands. Dots mark the perturbed lines P(15), P(20) and P(22).

(5).—The (1, 1) band, showing doubling and perturbations. The lines marked are R(12) and P(14), at which the doubling begins abruptly.

(6).—First part of the (3, 3) band, showing the single missing line.

(7).—First part of the (5, 4) band. The minimum at the null-line is partly obscured by the lines of the R branch returning from the head.

(8).—The (0, 0) band and the head of the overlapping (6, 5) band. The very faint double head of the (0, 0) band lies at the extreme left. An apparent discontinuity in intensity slightly to the right of the iron line is due to the presence of the (10, 8) band.


1.
(3,2)
(4,3)
(5,4)
2.
(0,0)
(6,5)
(1,1)
(2,2)
(3,3)
3.
(4,4)
(5,5)
(6,6)
4.
(4,4)
(4,3)
5.
(1,1)
6.
(3,3)
7.
(5,4)
8.
(0,0)

following way. Let the constant to be added to $n$ be unknown, and let its value be determined, together with the corresponding probable error, directly from the data. If the comparatively inaccurate values from the (2, 2) bands be omitted, one obtains

$$E_n = f(n + c) ; \quad c = + 0\cdot 504 \pm 0\cdot 010.$$

The agreement is significant not only as a quantitative verification of the theoretical isotope effect on the basis of the new mechanics, but also as an experimental justification for the use of $(n + \frac{1}{2})$ in the higher power terms of equation (8). It is not at once obvious how sensitive a test this affords for deciding the question. However, if it is assumed, for example, that $(n + \frac{1}{2})$ occurs only in the linear term, and $n$ in all higher terms, the agreement is not nearly as good. The algebraic sum of the deviations (observed minus calculated), which was previously $+ 0\cdot 28$ cm.$^{-1}$, then becomes $+ 1\cdot 80$ and the deviations show a very definite trend. Therefore it seems very probable that the vibrational energy should be expressed as a power series of $(n + \frac{1}{2})$, according to equation (8).

In conclusion, the writers wish to express their thanks to Profs. F. W. Loomis and R. S. Mulliken for suggestions and helpful criticism during the progress of this investigation.

## *Summary.*

(1) The violet SiN band spectrum excited by active nitrogen has been photographed with high dispersion, and measurements of the structure lines of the 10 strongest bands are tabulated.

(2) Each band has a doublet P and a doublet R branch, and there is one missing line, in complete accord with the theoretical predictions for a band system of the $^2S \rightarrow {}^2S$ type.

(3) Several perturbations are found in the rotational terms of the initial state. One of these is of a new type, since it affects markedly the rotational doubling of succeeding lines.

(4) The combination relations between P and R lines are applied to find the term-differences, from which the rotational constants are evaluated.

(5) The band-origins are determined, and an equation is derived for these, which gives the vibrational energy in the initial and final states.

The isotope effect is well marked for $Si^{28}N$, $Si^{29}N$, and $Si^{30}N$.

(6) From this effect in three bands of the strongest sequence, quantitative evidence is adduced in support of the quantum mechanics expression for the vibrational energy, which is developed in powers of $(n + \frac{1}{2})$.

# *The Difference between the Mechanical and Optical Lengths of a Steel End-Gauge.*

By F. H. Rolt and H. Barrell, National Physical Laboratory.

(Communicated by Sir Joseph Petavel, F.R.S.—Received August 30, 1928.)

## (1) *Introductory Notes.*

The two lapped surfaces whose separation defines the length of a good end-gauge or block-gauge generally approach a degree of optical flatness and parallelism sufficient for their use in interferometry. If, therefore, such a gauge is supported between the semi-transparent mirrors of a Fabry-Perot étalon of greater length than the gauge, with its surfaces parallel to the mirrors, the gauge may be standardised in terms of light waves by the methods usually applied to Fabry-Perot étalons.

In fig. 1 L is the optical separation of the étalon mirrors, $l_1$ and $l_2$ are respectively the optical separations of a gauge surface and an adjacent étalon mirror at each end of the figure, and O is the optical length of the gauge: therefore

$$O = L - (l_1 + l_2), \tag{1}$$

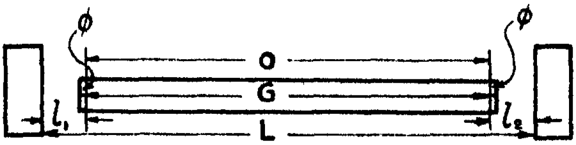


Fig. 1.

L is measured either directly or indirectly in terms of light waves, the choice depending upon the magnitude of L, while both $l_1$ and $l_2$ are measured directly in terms of light waves by observation of the reflected system of circular interference fringes; thus O may be obtained in terms of light waves.

It is generally supposed that when light is reflected in air at glass or quartz surfaces a change of phase equal to $\pi$ takes place, and that the optical and geometrical surfaces of glass and quartz are coincident. But when light is reflected in air at a metallic surface there is an additional change of phase $p$ which constitutes a phase loss. This phase loss varies slightly with the wave-length of light but may be considered as constant for all practical purposes. It has an effect upon optical measurements, where steel gauge surfaces are used as reflectors, which is equivalent to an apparent displacement of the reflecting surfaces from the geometrical surfaces towards the interior of the gauge. In other words light appears to penetrate a metallic surface (fig. 2) and is apparently reflected at a plane which is parallel to the geometrical surface, but is displaced from it by an amount $\phi$, where

$$\phi = \tfrac{1}{2}p\lambda.$$

$\lambda$ is the wave-length of the incident light so that $\phi$ varies for different colours.

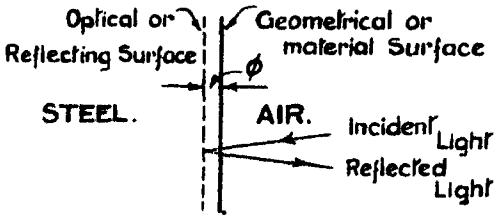

Optical or Reflecting Surface
Geometrical or material Surface
$\phi$
STEEL.
AIR.
Incident Light
Reflected Light

FIG. 2.

If $\phi$ in fig. 1 is the apparent displacement at a lapped steel surface for light of given wave-length, the optical length O of an end-gauge in terms of this radiation is less than the geometrical separation G of its parallel surfaces by an amount equal to $2\phi$, *i.e.*,

$$O = G - 2\phi. \tag{2}$$

It is important to note here that the geometrical length G of an end-gauge is not equivalent to the measured value M of its length as determined by the mechanical method of standardisation.* In the mechanical standardisation the quantity measured is the geometrical length G augmented by the thickness $t'$ of the wringing film formed between two lapped surfaces in wringing contact, *i.e.*,

$$M = G + t'$$

Let G be eliminated from these two equations, then

$$M = O + (2\phi + t'). \tag{3}$$

Thus, if the value of $(2\phi + t')$ in terms of light waves is known, it is possible to derive the actual value in terms of light waves of the length of an end-gauge, as it would be measured by mechanical standardisation, from a purely optical measurement of the type outlined above.

One of the stages in the procedure contemplated for the establishment of a wave-length standard of length involves the measurement, in terms of light waves, of a steel end-gauge having parallel, lapped measuring faces, and 1 metre or 1 yard in length. Since it is essential for practical usage to standardise the M (or mechanical) value of the gauge, an accurate knowledge of the correction $(2\phi + t')$ is required. Pérard and Maudet* have given the mean value of $(2\phi + t')$ as $0{\cdot}086\ \mu$ or $3{\cdot}4 \times 10^{-6}$ inch for wave-lengths of the visible spectrum between $0{\cdot}61\ \mu$ and $0{\cdot}44\ \mu$. The measurement of the quantity $(2\phi + t')$ has been repeated in the Metrology Department of the National Physical Laboratory by a method similar in principle to that used by Pérard and Maudet, though differing somewhat in detail.

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* Sears, 'Proc. Roy. Inst.,' vol. 25, p. 112 (1926).

### (2) *General Description of Method.*

The procedure which entails the introduction of the correction $(2\phi + t')$ can also be utilised to measure the value of the correction. Suppose that the optical lengths of a series of $n$ short block-gauges are measured by the scheme outlined in fig. 1. It is necessary to have means of adjusting the gauge surfaces and semi-transparent mirrors into parallelism with one another.

From fig. 1 the optical length O of a gauge is given by the expression

$$\mathrm{O} = \mathrm{G} - 2\phi$$

where G and $\phi$ have the meanings already assigned to them. If $n$ gauges are measured, then

$$\left.\begin{aligned} \mathrm{O}_1 &= \mathrm{G}_1 - 2\phi \\ \mathrm{O}_2 &= \mathrm{G}_2 - 2\phi \\ \ldots &= \ldots\ldots\ldots \\ \mathrm{O}_n &= \mathrm{G}_n - 2\phi \end{aligned}\right\} . \tag{4}$$

It is assumed that the value of $\phi$ is the same for all the gauge surfaces concerned.

From equations (4)

$$\Sigma\,[\mathrm{O}] = \Sigma\,[\mathrm{G}] - 2n\phi \tag{5}$$

where

$\Sigma\,[\mathrm{O}]$ = sum of optical lengths $\mathrm{O}_1$, etc.

$\Sigma\,[\mathrm{G}]$ = sum of geometrical lengths $\mathrm{G}_1$, etc.

Now suppose that a combination is formed from the $n$ gauges wrung together and that its optical length O′ is measured in the same way, then

$$\mathrm{O}' = \Sigma\,[\mathrm{G}] + (n-1)t' - 2\phi, \tag{6}$$

where $t'$ is the separation of two lapped surfaces when wrung together.

From equations (5) and (6)

$$\mathrm{O}' - \Sigma\,[\mathrm{O}] = (n-1)(2\phi + t')$$

or

$$(2\phi + t') = \frac{\mathrm{O}' - \Sigma\,[\mathrm{O}]}{(n-1)} . \tag{7}$$

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* 'Trav. et Mém. Bureau Internat.,' vol. 17, p. 54 (1921).

The expression $(2\phi + t')$ represents (equation (3)) the difference between the mechanical and optical lengths of an end-gauge, and therefore its value may be derived from purely optical measurements of the type described upon a series of short block-gauges, assuming that the lapped surfaces of these gauges possess optical qualities which are a fair representation of the optical qualities of lapped surfaces of end-gauges in general.

### (3) *Experimental Notes.*

The two semi-transparent mirrors were arranged parallel to one another by wringing them to the ends of a pair of 1-inch block gauges, differing in length by about two-millionths of an inch. In the first instance each gauge or combination of the series of short block gauges whose optical lengths were required was supported on a bracket between the semi-silvered faces of the mirrors. This bracket was part of a framework which was capable of small adjustments about horizontal and vertical axes, and was used to bring the faces of the gauges it supported into parallelism with the semi-transparent mirrors. It was soon found that heavy machinery running in the Laboratory kept the bracket in continual vibration, although the apparatus was mounted on an insulated concrete bench. The idea of mounting the gauges upon an adjustable bracket therefore had to be abandoned.

After many trials an arrangement was adopted in which the gauge or combination to be optically measured, the semi-transparent mirrors, and the 1-inch separators were all wrung together, so that no relative movement of the parts could take place.

In fig. 3 the mirrors A and B are wrung to the ends of a pair of 1-inch gauges

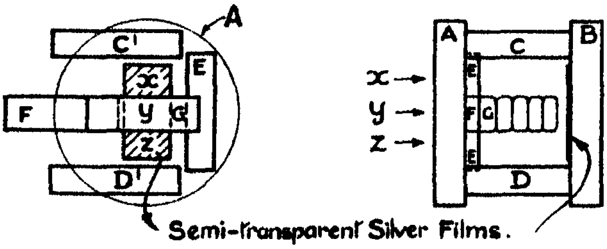

FIG. 3.

C and D, so that the rectangular semi-transparent films (1 inch × ⅛ inch) face one another. The semi-silvered face of A is shown in plan. C′ and D′ are areas on A which are brought into wringing contact with the separating gauges, while E and F represent two ⅛-inch gauges, differing in length by less than

$1 \times 10^{-6}$ inch, that are in wringing contact with A in the positions indicated. Because of the limited surfaces of the mirrors A and B, the gauges C and D are wrung to them somewhat unsymmetrically in order that E and F may occupy convenient positions on A. A gauge or combination, G, to be optically measured is wrung across the upper surfaces of E and F so that it bridges the semi-silvered surface of A. If all the gauges are suitably chosen with respect to length and parallelism the surfaces of G are approximately parallel to the semi-transparent mirrors.

A series of six ⅛-inch gauges was used for the measurements. The optical length of a single gauge or combination of this series was measured by observing the optical separation of the semi-transparent mirrors and subtracting from this the sum of the optical separations of the surfaces of the gauge or combination from adjacent surfaces of the mirrors.

A diagram of the optical system is shown in fig. 4. The interferometer I is supported at the edges of its semi-transparent mirrors on a V-block. The V-block rests on a circular surface plate capable of exact rotation in its own plane, the rotation being limited to 180° by adjustable stops. Levelling screws are provided for the rotating table, and they stand on a plate having a traversing motion at right angles to the direction of the incident beam of light.

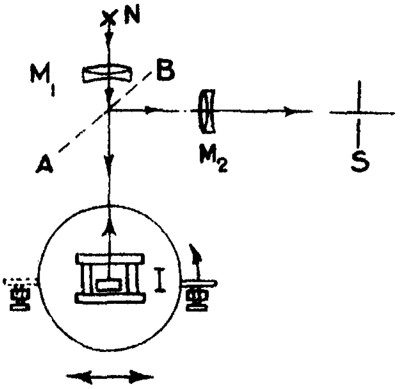

Fig. 4.

The source of light is a neon tube N viewed broadside-on and excited by a discharge from an induction coil. A convergent beam from the source is directed by the lens $M_1$ through the semi-transparent mirror AB to the interferometer. Light reflected by the interferometer is again partially reflected at AB and the interference fringes produced in this light are focussed on the slit S of a constant deviation spectroscope by an achromatic lens $M_2$. Suitable operation of the traversing and rotating motions of the interferometer support then brings fringes due to each of the optical separations $L_1$, $L_2$, $l_1$ and $l_2$ (fig. 5) on to the slit of the spectroscope. The optical system and the levelling screws of the interferometer support are adjusted so that the centre of each system of circular fringes is focussed on the same point of the slit. This adjustment is made once and for all before measurements are commenced.

The gauge or combination represented by G in figs. 3 and 5 was only measured at its centre "*y*." A preliminary experiment without G in position correlated

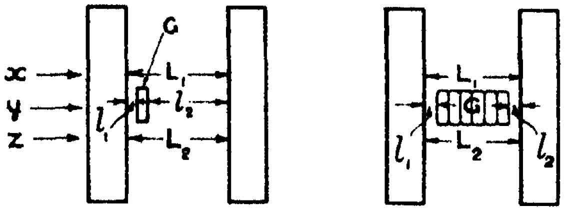

FIG. 5.

the mean of the optical separations $L_1$ and $L_2$ at the positions "*x*" and "*z*" with the optical separation L at "*y*." It was found that the mean of $L_1$ and $L_2$ was less than L by $0 \cdot 2 \times 10^{-6}$ inch. Since the small difference between $L_1$ and $L_2$ was also constant in sign and magnitude whether G was a single gauge or combination, it was assumed that the relation between L, $L_1$ and $L_2$ given above always held.

The interferometer was shielded from draughts by a well-lagged enclosure of cardboard. The temperature inside the enclosure during a set of observations usually tended to rise steadily, and it was necessary to take a symmetrical series of observations in order to compensate for this effect. Referring to fig. 5, the observations for $L_1$ and $l_1$ were taken in succession. The interferometer was then turned through 180° and the observations for $l_2$ and $L_2$ taken in succession. The order was then reversed, starting at $L_2$ and finishing at $L_1$. Each distance was thus measured twice, and the means corresponded to values at the same mean time and temperature if the observations were taken at a constant rate, and the temperature changed uniformly in one direction. Temperature readings were taken regularly during the time occupied in observing the fringes, and the barometric pressure and humidity were noted at the beginning, middle and end of this period.

Measurements of the linear diameters of the circular fringes were made visually, using a micrometer eyepiece fitted to the spectroscope. In some cases the diameters of three rings in six neon radiations between λ 5852 and λ 6507 were observed for each of the quantities $L_1$, $l_1$, $l_2$ and $L_2$. In others only the two extreme radiations of this group were utilised, since the approximate orders of interference were well established, *i.e.*, $L_1$ and $L_2$ were each 1 inch, $l_1$ was $\frac{1}{8}$ inch, and $l_2$ was $\frac{3}{4}$ inch if a single $\frac{1}{8}$-inch gauge was being measured, or $\frac{1}{8}$ inch if a combination of six $\frac{1}{8}$-inch gauges was being measured. The fractional order of interference (or excess fraction) at the centre of each system of fringes was calculated from the linear diameters of fringes by a least square method, which is described in the Appendix. Then with the aid of the well-known method of coincidences the total order of interference for each radiation was derived, and hence the values of the quantities $L_1$, $l_1$, $l_2$ and $L_2$ could be calculated, since the wave-lengths of the radiations were known. Corrections were applied for the effect of variations of the refractive index of the air upon the standard values of the wave-lengths. In calculating the values of O and O′ by equation (1) the above-mentioned correction of $+0{\cdot}2 \times 10^{-6}$ inch was applied to the mean of $L_1$ and $L_2$ in order to obtain the true value of L.

The pair of semi-transparent mirrors and the mirror AB (fig. 4) were silvered by the method of cathodic sputtering in a vacuum. It was found that the best conditions were realised when the silver films possessed approximately equal reflecting and transmitting powers.

The combination of six gauges was measured ten times. After each measurement the combination was broken down, the gauge surfaces cleaned with the usual mixture of alcohol, ether and ammonia, and then wrung together again with a minimum quantity of paraffin oil. Care was always taken to have the portions of the terminal surfaces where light was reflected as clean as possible. The combination was left for at least 2 hours in the apparatus before it was measured. Single gauges were measured three times each, and after each measurement were taken out of the interferometer, cleaned, and then re-wrung to the upper surfaces of E and F (fig. 3).

### (4) *Results.*

Table I shows the results of optical measurements of the ¾-inch combination of six ⅛-inch gauges, reduced to values at a mean temperature of 18·40° C. with the aid of a coefficient of expansion derived from optical measurements of the combination at temperatures ranging from 16° C. to 19·5° C. The optical lengths were calculated from measurements in two neon radiations, $\lambda_1 = 5852{\cdot}488$ Å and $\lambda_6 = 6506{\cdot}528$ Å,* the conversion factor of 1 metre = 39·370147† inches being used to give the results in inch units. The values are actually expressed in terms of errors from the nominal size (¾ inch) of the combination in units of one-millionth of an inch.

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* 'Bull. Bur. Stand.,' vol. 14, p. 765 (1918).

† 'Phil. Trans.,' A, vol. 227, p. 281 (1928).

Table I.—Optical Lengths at 18·40° C. of the Combination in Terms of Two Neon Radiations.

Nominal size = $\frac{3}{4}$ inch. Unit of error = $1 \times 10^{-6}$ inch.

| Observation. | $\lambda_1$. | $\lambda_6$. |
|---|---|---|
| 1 | −56·2 | −56·8 |
| 2 | −51·0 | −53·5 |
| 3 | −56·9 | −57·7 |
| 4 | −49·8 | −51·2 |
| 5 | −49·0 | −49·8 |
| 6 | −49·1 | −50·2 |
| 7 | −51·6 | −52·0 |
| 8 | −55·4 | −56·7 |
| 9 | −54·2 | −55·6 |
| 10 | −54·1 | −55·4 |
| Means ... | −52·8 | −53·9 |

The mean values of the optical lengths of the combination at 18·40° C. are:—

$$O' = \tfrac{3}{4} \text{ inch} - 52 \cdot 8 \times 10^{-6} \pm 2 \cdot 8 \times 10^{-6} \text{ for } \lambda_1,$$
$$O' = \tfrac{3}{4} \text{ inch} - 53 \cdot 9 \times 10^{-6} \pm 2 \cdot 8 \times 10^{-6} \text{ for } \lambda_6.$$

The uncertainty indicated for these two results is obtained by calculating the probable effect of the variations in Table I upon the arithmetic means.

Table II shows the values of the optical lengths at 18·40° C. of the series of single gauges whose nominal lengths are $\frac{1}{8}$ inch.

Table II.—Optical Lengths at 18·40° C. of the Series of Single Gauges in Terms of Two Neon Radiations.

Nominal size = $\frac{1}{8}$ inch. Unit of error = $1 \times 10^{-6}$ inch.

| Gauge. | Wave-length. | (1). | (2). | (3). | Means. |
|---|---|---|---|---|---|
| $\frac{1}{8}$-inch No. 10 ............ | $\lambda_1$ | −13·9 | −14·2 | −14·0 | −14·0 |
| | $\lambda_6$ | −14·3 | −15·4 | −14·8 | −14·8 |
| $\frac{1}{8}$-inch No. 11 ............ | $\lambda_1$ | −14·0 | −13·4 | −14·0 | −13·8 |
| | $\lambda_6$ | −14·4 | −15·0 | −14·8 | −14·7 |
| $\frac{1}{8}$-inch No. 12 ............ | $\lambda_1$ | −14·3 | −14·5 | −14·8 | −14·5 |
| | $\lambda_6$ | −14·9 | −14·5 | −14·8 | −14·7 |
| $\frac{1}{8}$-inch No. 13 ............ | $\lambda_1$ | −15·3 | −15·5 | −16·3 | −15·7 |
| | $\lambda_6$ | −15·6 | −16·3 | −17·4 | −16·4 |
| $\frac{1}{8}$-inch No. 14 ............ | $\lambda_1$ | −13·4 | −13·3 | −14·2 | −13·6 |
| | $\lambda_6$ | −15·0 | −14·3 | −15·1 | −14·8 |
| $\frac{1}{8}$-inch No. 15 ............ | $\lambda_1$ | −14·2 | −13·7 | −13·5 | −13·8 |
| | $\lambda_6$ | −14·6 | −14·0 | −13·8 | −14·1 |

The sums of the optical lengths of the series of single gauges for the two radiations are :—

$$\Sigma[O] = \tfrac{3}{4} \text{ inch} - 85{\cdot}4 \times 10^{-6} \pm 0{\cdot}5 \times 10^{-6} \text{ for } \lambda_1.$$

$$\Sigma[O] = \tfrac{3}{4} \text{ inch} - 89{\cdot}5 \times 10^{-6} \pm 0{\cdot}5 \times 10^{-6} \text{ for } \lambda_6.$$

The uncertainty indicated for these two results is obtained by calculating the probable effects of the variations in Table II upon the arithmetic means.

By equation (7) :

$$(2\phi + t') = (O' - \Sigma[O])/5$$

since $n = 6$.

Substituting the values of $O'$ and $\Sigma[O]$ for $\lambda_1$ and $\lambda_6$ in this equation, then :—

$$(2\phi + t') = 6{\cdot}5 \times 10^{-6} \pm 0{\cdot}6 \times 10^{-6} \text{ inch for } \lambda_1.$$

$$(2\phi + t') = 7{\cdot}1 \times 10^{-6} \pm 0{\cdot}6 \times 10^{-6} \text{ inch for } \lambda_6.$$

Thus the mean value of $(2\phi + t')$ for the red and yellow regions of the visible spectrum is $6{\cdot}8 \times 10^{-6} \pm 0{\cdot}6 \times 10^{-6}$ inch or $0{\cdot}173\ \mu \pm 0{\cdot}014\ \mu$. Pérard and Maudet (*loc. cit.*) give a mean value $0{\cdot}086\ \mu$ or $3{\cdot}4 \times 10^{-6}$ inch for $(2\phi + t')$ for visible radiations extending from the red to the blue regions.

Pérard and Maudet also measured directly the value of $\phi$ alone and thus by calculation derived a value of $t'$ equal to $-0{\cdot}06\ \mu$.

In the Metrology Department of the National Physical Laboratory, an independent measurement of $t'$ has been made,* giving a probable value of $+0{\cdot}005\ \mu$ or $0{\cdot}2 \times 10^{-6}$ inch. Taking this value in conjunction with the above determined value of $(2\phi + t')$, the calculated value of $\phi$ is found to be $0{\cdot}084\ \mu$ or $3{\cdot}3 \times 10^{-6}$ inch, as against the measured value of Pérard and Maudet (*loc. cit.*, p. 74) $0{\cdot}079\ \mu$ or $3{\cdot}1 \times 10^{-6}$ inch for a similar region of the spectrum. Good agreement is obtained therefore between the value of $\phi$ calculated from the National Physical Laboratory measurements and the directly measured value given by Pérard and Maudet. With regard to the value of $t'$, no results have been obtained which confirm the apparent value of $-0{\cdot}06\ \mu$ derived by Pérard and Maudet, and it is difficult to believe in such a value.

The value obtained for $(2\phi + t')$ by the work described in this paper is also closely confirmed by direct comparison of the measured lengths of the individual gauges, made by optical and mechanical methods respectively. In the following table the sizes are expressed in terms of errors from nominal size.

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* 'Roy. Soc. Proc.,' A, vol. 116, p. 401 (1927).

Table III.—Comparison of Optical and Mechanical Lengths of Gauges at 16·67° C.

Nominal size = $\frac{1}{8}$ inch. Unit of error = $1 \times 10^{-6}$ inch.

| Gauge number. | Optical values at 16·67° C. | | Mechanical values at 16·67° C. | (M − O) = ($2\phi + t'$). | |
|---|---|---|---|---|---|
| | $\lambda_1$. | $\lambda_6$. | | $\lambda_1$. | $\lambda_6$. |
| 10 | −16·8 | −17·6 | −11·1 | 5·7 | 6·5 |
| 11 | −16·6 | −17·5 | −9·3 | 7·3 | 8·2 |
| 12 | −17·3 | −17·5 | −10·9 | 6·4 | 6·6 |
| 13 | −18·5 | −19·2 | −12·1 | 6·4 | 7·1 |
| 14 | −16·4 | −17·6 | −10·6 | 5·8 | 7·0 |
| 15 | −16·6 | −16·9 | −10·7 | 5·9 | 6·2 |
| | | | Means .... | 6·2 | 6·9 |

The mean of the differences (M − O) is $6 \cdot 6 \times 10^{-6}$ inch, as compared with $6 \cdot 8 \times 10^{-6}$ inch derived above from purely optical measurements. The closeness of this agreement is no doubt somewhat fortuitous but it is at least additional evidence in favour of the new value obtained for $(2\phi + t')$.

### (5) *Conclusion.*

It was mentioned in section (1) that if $p$ is the phase loss for light of wave-length $\lambda$ when reflected at a lapped steel surface then $\phi = \frac{1}{2}p\lambda$. Substituting in this equation the calculated value for $\phi$ of 0·084 μ for a mean wave-length of 0·618 μ, then $p = 0 \cdot 272$. The value given by Pérard and Maudet for the same region of the spectrum is $p = 0 \cdot 258$, and these observers state that $p$ is practically constant for yellow and red light, but its value increases appreciably in the region of shorter wave-lengths. Therefore, on the basis of the work described in this paper, the values of (M — O) may be calculated for all visible radiations of greater wave-length than 0·55 μ by means of the following equation

$$(M - O) = (2\phi + t') = 0 \cdot 27\,\lambda + 0 \cdot 005\,\mu$$

where $\lambda$ is expressed in microns.

## APPENDIX.

### *Calculation of Excess Fractions by a Method of Least Squares.*

The theory of the Fabry-Perot étalon has been recently described in a concise manner by Childs.[*] For the purposes of this Appendix, it is sufficient to indicate that the normal distance, $t$, between the optical surfaces of the étalon can be expressed in the following form :—

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[*] 'J. Sci. Insts.,' vol. 3, pp. 97, 129 (1926).

$$2t = (\mathrm{N} + \varepsilon)\,\lambda \qquad (1)$$

where $\lambda$ is the wave-length of a monochromatic radiation and $(\mathrm{N} + \varepsilon)$ is the total number of waves of this radiation contained in the distance $2t$, N being an integer and $\varepsilon$ the excess fraction.

In the foregoing work a real image of the circular fringe systems is projected on the slit of a spectroscope by the lens $\mathrm{M}_2$ (fig. 4) and the linear diameters of the circular fringes* are measured visually in the focal plane of the spectroscope, using a micrometer eyepiece. It can be shown (Childs, *loc. cit.*) that if $d_1, d_2, d_3, \ldots, d_p$ are the linear diameters of the first $p$ fringes, counting outwards from the centre of the system, then the following relations exist between the squares of the linear diameters and $\varepsilon$ :—

$$\varepsilon = k\mathrm{N}d_1^2, \quad 1 + \varepsilon = k\mathrm{N}d_2^2, \quad 2 + \varepsilon = k\mathrm{N}d_3^2, \ldots, \quad (p-1) + \varepsilon = k\mathrm{N}d_p^2. \quad (2)$$

In these equations $k$ is a constant whose value depends on the focal length of the lens $\mathrm{M}_2$ (fig. 4) and the magnification factor of the spectroscope.

The fractional excess $\varepsilon$ may therefore be calculated from measurements of the linear diameters (in any arbitrary units) of only two fringes, since there are only two unknown quantities, $\varepsilon$ and $k\mathrm{N}$. A more accurate value of $\varepsilon$ can obviously be derived if more than two fringes are measured. Suppose $p$ fringes are measured and that in equations (2) we put :—

$$\varepsilon/k\mathrm{N} = a\,; \quad 1/k\mathrm{N} = b.$$

Then rewriting equations (2)

$$d_1^2 = a, \quad d_2^2 = a + b, \quad d_3^2 = a + 2b, \ldots, \ldots, \quad d_p^2 = a + (p-1)\,b,$$

the best values for $a$ and $b$ can be determined by a method of least squares.

The normal equations in $a$ and $b$ are

$$\Sigma = pa + sb,$$
$$\mathrm{S} = sa + \sigma b,$$

where

$$\Sigma = d_1^2 + d_2^2 + d_3^2 + \ldots + d_p^2,$$
$$\mathrm{S} = d_2^2 + 2d_3^2 + 3d_4^2 + \ldots + (p-1)\,d_p^2,$$
$$s = 1 + 2 + 3 + \ldots + (p-1),$$
$$\sigma = 1^2 + 2^2 + 3^2 + \ldots + (p-1)^2.$$

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* Since the interference effects are viewed in light reflected from the interferometer in the above work, the dark fringes are measured. The fringe systems produced in transmitted and reflected light by a Fabry-Perot étalon having lightly silvered reflecting surfaces are analogous to Newton's Rings in transmitted and reflected light.

Solving for $a$ and $b$

$$a = \frac{\sigma\Sigma - sS}{p\sigma - s^2}, \qquad b = \frac{pS - s\Sigma}{p\sigma - s^2}.$$

Therefore

$$\varepsilon = \frac{a}{b} = \frac{\sigma\Sigma - sS}{pS - s\Sigma}. \tag{3}$$

It is customary at the Laboratory to measure five fringes, but for the present work it was considered sufficient to measure three. If $p = 3$, then

$$\varepsilon = \frac{5\Sigma - 3S}{3S - 3\Sigma}.$$

It often happens that the first fringe is too small and indistinct for accurate measurement, but the same method may be applied to the diameters of the next $p$ rings, and the right-hand side of equation (3) then automatically gives the value of $(1 + \varepsilon)$.

The writers wish to thank Sir Joseph Petavel and Mr. J. E. Sears for their encouragement and for facilities for carrying out the experiments at the National Physical Laboratory.

# *Ground-Terms in the Spectrum of Nickel II and Proposed Standard Wave-Lengths in the Schumann Region.*

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(Communicated by R. Whiddington, F.R.S.—Received August 31, 1928.)

[Plate 6.]

During the investigation of fuse-spectra* it has been observed that this source is particularly suited to the study of low-level terms. When the fuse is blown in air, reversals occur owing to the vapour produced, and these reversed lines are found to involve low-level terms. When the fuse is blown *in vacuo* in the vacuum grating spectrograph, it is found that the lines involving the ground-terms of the spark spectrum come out particularly strongly, and are also very long (see note on the spectra of Cu II and Ag II at the end of this paper, and spectra 1 and 2 in Plate 6).

Since the expected ground-terms $^2D_3$ and $^2D_2$ of Ni II have not yet been found, it was decided to see what information the above-mentioned methods could yield.

### *Terms in the Spectrum of* Ni II.

The spectrum of the once-ionised atom of nickel has been recently analysed into terms by A. G. Shenstone.† In this scheme, which accords with the principles of Hund, there are missing the expected ground-terms $^2D_3$ and $^2D_2$, the low-level term $^2S_1$, and the intermediate terms $^2P_2$, $^2P_1$. Shenstone estimates the D-terms at about 5000 to 10,000 cm.$^{-1}$ below the term $a\,^4\overline{F}_5$, which, being the lowest term he has found, he calls zero. On this basis, therefore, the missing D-terms will be negative. In what is to follow, it will be shown that these D-terms have the values provisionally fixed at $-8392\cdot9$ and $-6886\cdot0$ for $^2D_3$ and $^2D_2$ respectively, so that they agree well with the limit so set by Shenstone in his estimate. It will be observed that the terms are "inverted," *i.e.*, that the lower term is the one having the higher $j$-number—in agreement with the rule requiring atoms in the right-hand half of the periodic table to have inverted terms.

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* Menzies, 'Roy. Soc. Proc.,' A, vol. 117, p. 88 (1928), and vol. 119, p. 249 (1928).

† 'Phys. Rev.,' vol. 30, p. 255 (1927).

### *Experimental Procedure.*

The spectrograms were obtained in the Schumann region by the method outlined in the author's second paper referred to above, and will consequently be only briefly described here.

Wires of commercial nickel, 24 gauge, were mounted in front of the slit of a vacuum grating spectrograph, made by Hilger, having a concave N.P.L. grating of 1 metre radius, ruled with a grating interval of 0·0000694158 cm. The spectrograph was exhausted by a two-stage glass mercury-vapour pump, backed by a Cenco-Hyvac oil-pump (small size). After the pumps had sufficiently reduced the pressure, the wires were fused, and the very brief flash so caused automatically recorded the spectrum on the plate, in position, in the spectrograph.

In the present work, two improvements were introduced. First, the wires were mounted horizontally, instead of vertically, and the chamber carrying them was so modified that they were nearer to the slit (about 2 cm. distant). It was found that, under these circumstances, the lines varied greatly in length, in spite of the astigmatic action of the grating, so allowing the application of the method of long and short lines. This has been earlier observed by Simeon.*

Secondly, the spring-switch which was formerly used to close the circuit was discarded, and, instead, the wires were themselves used as a switch. This was effected by lining up one wire carefully, held in an ebonite plug, while the other wire was held in a bung of pliant rubber, and arranged initially so as not quite to make contact. A slight tweak was then sufficient to cause the fuse. The same accumulator-battery of 110 volts, 144 ampere-hour capacity, was used, as before.

The slit-width was at first 1/10th mm. wide but it was later reduced to 1/30th mm. In spite of this, it was still possible to get a good spectrogram with only one fuse, and the lines were very much sharper. (That reproduced in the plate was taken with the slit 1/10th mm. wide.)

### *Measurement of Wave-lengths.*

This was done by interpolation between the carbon lines which occur as impurity lines in all spectrograms taken in this region, together with the hydrogen line at 1215·68 A.U. (first line of the Lyman series). The values of the carbon lines were taken as those given by Smith and Lang,† supplemented by those of Bowen* above 1560. The values thus obtained were probably accurate to 0·1 A.U., except in the cases of diffuse or very faint lines, and in some cases where the lines were sharp and near to a standard line the error was probably much less than this.

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* 'Roy. Soc. Proc.,' A, vol. 104, p. 368 (1923).

† 'Phys. Rev.,' vol. 27, p. 36 (1926).

### *Results.*

In the Table I which follows, the first column gives the wave-length *in vacuo*, the second remarks on the appearance of the line (d, diffuse ; s, strong ; w, weak ; l, long ; m, medium ; sh, short ; and c, complex ; *i.e.*, that the

Table I.

| Wave-length. | Remarks. | Wave-length (Bloch). | Wave-number. | Terms. | Wave-number (calculated). |
|---|---|---|---|---|---|
| 1164·5 | s | | 85877 | | |
| 1168·0 | w | | 85617 | | |
| 1171·3 | w | | 85376 | | |
| 1173·4 | w | | 85220 | | |
| 1206·3 | w | | 82898 | | |
| 1298·82 | sh | | 76993·0 | | |
| 1317·20 | l | | 75918·6 | ${}^2D_3 - c\,{}^2F_4$ | 75916·9 |
| 1323·87 | sh d | | 75536·1 | | |
| 1347·70 | sh w | | 74200·5 | | |
| 1360·70 | sh w | | 73491·6 | | |
| 1362·09 | sh w | | 73416·6 | | |
| 1370·21 | l | 1370·31 | 72982·6 | ${}^2D_3 - c\,{}^2P_2$ | 72984·0 |
| 1374·14 | ml | 1374·15 | 72772·8 | ${}^2D_2 - c\,{}^2\overline{S}_1$ | 72774·9 |
| 1375·63 | d f | | 72694·0 | | |
| 1381·38 | l | 1381·44 | 72391·4 | ${}^2D_2 - c\,{}^2P_1$ | 72394·6 |
| 1393·37 | ml | | 71768·5 | ${}^2D_3 - c\,{}^2\overline{D}_3$ | 71769·7 |
| 1396·10 | sh | 1396·12 | 71628·1 | | |
| 1398·89 | ml | 1398·82 | 71485·3 | ${}^2D_2 - c\,{}^2P_2$ | 71477·1 |
| 1402·84 | sh d | | 71284·0 | | |
| 1411·09 | l | 1411·07 | 70867·2 | ${}^2D_2 - c\,{}^2\overline{D}_2$ | 70867·0 |
| 1412·91 | sh | | 70775·9 | ${}^2D_3 - b\,{}^4\overline{D}_4$ | 70776·2 |
| 1415·80 | sh | 1415·60 ? | 70631·5 | ${}^2D_3 - b\,{}^4\overline{D}_3$ | 70634·0 |
| 1420·61 | sh | 1420·28 ? | 70399·7 | | |
| 1423·04 | d w | 1423·02 | 70272·1 | ${}^2D_2 - c\,{}^2\overline{D}_3$ | 70262·8 |
| 1428·97 | sh | 1428·80 | 69980·5 | | |
| 1434·19 | sh | 1434·15 | 69725·8 | | |
| 1445·06 | sh w | | 69201·3 | ${}^2D_2 - b\,{}^4\overline{D}_2$ | 69198·5 |
| 1446·69 | sh w | 1446·47 | 69123·3 | ${}^2D_2 - b\,{}^4\overline{D}_3$ | 69127·1 |
| 1449·86 | d sh w | | 68972·2 | ${}^2D_3 - b\,{}^2P_2$ | 68964·3 |
| 1454·93 | l | 1454·75 | 68731·8 | ${}^2D_3 - b\,{}^2\overline{D}_3$ | 68734·1 |
| 1463·48 | l d w | | 68330·3 | | |
| 1467·79 | l | | 68129·6 | ${}^2D_3 - b\,{}^2F_4$ | 68129·8 |
| 1482·13 ? | d w | | 67470·5 | ${}^2D_2 - b\,{}^2P_2$ ? | 67457·4 |
| 1500·46 | l | 1500·38 | 66646·2 | ${}^2D_2 - b\,{}^4\overline{D}_2$ | 66646·0 |
| 1502·22 | l | 1502·14 | 66568·1 | ${}^2D_3 - b\,{}^4P_3$ | 66569·7 |
| 1510·84 | l | 1510·85 | 66188·6 | ${}^2D_2 - b\,{}^2F_3$ | 66186·1 |
| 1536·94 | l | 1536·79 | 65064·3 | ${}^2D_2 - b\,{}^4P_3$ | 65062·8 |
| 1581·39 | sh s | 1581·29 | 63235·5 | $a\,{}^4F_2 - c\,{}^2P_1$ | 63238·5 |
| 1605·57 | m | 1605·60 | 62283·2 | | |
| 1608·19 | m d | 1608·22 | 62181·7 | | |
| 1614·66 | m | 1614·65 | 61932·6 | | |

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* 'Phys. Rev.,' vol. 29, p. 238 (1927).

Table I—(continued).

| Wave-length. | Remarks. | Wave-length (Bloch). | Wave-number. | Terms. | Wave-number (calculated). |
|---|---|---|---|---|---|
| 1616·96 | l | 1616·92 | 61844·5 | | |
| 1629·02 | sh | 1628·92 | 61386·6 | | |
| 1631·89 | sh | 1631·92 | 61278·6 | | |
| 1649·64 | m | 1649·60 | 60619·3 | | |
| 1652·83 | m s c | 1652·72 | 60502·3 | $a\,{}^4\overline{F}_3 - b\,{}^4\overline{D}_3$? | 60519·3 |
| 1661·56 | m s | 1661·55 | 60184·4 | | |
| 1671·90 | sh | 1672·01 | 59812·2 | | |
| 1672·91 | sh | | 59776·1 | | |
| 1687·75 | m | | 59250·5 | | |
| 1690·59 | sh | 1690·55 | 59150·9 | | |
| 1692·44 | l | 1692·29 | 59086·3 | | |
| 1701·64 | sh d | 1701·43 | 58766·8 | | |
| 1703·45 | l | 1703·23 | 58704·4 | ${}^2D_3 - a\,{}^2\overline{D}_2$ | 58704·4 |
| 1704·67 | sh d | 1704·44 | 58662·4 | | |
| 1707·39 | m s | 1707·20 | 58568·9 | | |
| 1708·62 | m w | 1708·40 | 58526·8 | | |
| 1709·74 | l s | 1709·69 | 58488·4 | ${}^2D_3 - a\,{}^2F_3$ | 58491·8 |
| 1715·33 | m s | 1715·12 | 58297·8 | $a\,{}^4\overline{F}_2 - b\,{}^2P_2$ | 58301·3 |
| 1715·94 | sh s | 1715·82 | 58277·1 | | |
| 1719·50 | m s | 1719·27 | 58156·4 | | |
| 1721·24 | sh s | 1721·03 | 58097·7 | | |
| 1722·29 | m s | 1722·14 | 58062·2 | | |
| 1723·74 | sh w | 1723·70 | 58013·4 | $a\,{}^4\overline{F}_3 - b\,{}^2F_4$ | 58015·1 |
| 1724·41 | sh w | 1724·26 | 57990·8 | $a\,{}^2F_3 - c\,{}^2P_2$ | 57989·6 |
| 1733·18 | m | | 57697·4 | | |
| 1738·28 | m | 1738·21 | 57528·1 | | |
| 1738·77 | m | 1738·76 | 57511·9 | | |
| 1741·60 | l | 1741·61 | 57418·5 | ${}^2D_3 - a\,{}^2\overline{D}_3$ | 57418·5 |
| 1742·06 | m | 1742·10 | 57403·3 | | |
| 1747·02 | ml | 1746·94 | 57240·3 | $a\,{}^4F_4 - b\,{}^4P_3$ | 57240·4 |
| 1748·32 | l | 1748·31 | 57197·8 | ${}^2D_2 - a\,{}^2\overline{D}_2$ | 57197·5 |
| 1751·93 | l | | 57079·9 | ${}^2D_3 - a\,{}^2F_4$ | 57079·1 |
| 1753·05 | ml | 1753·22 | 57043·4 | | |
| 1754·82 | l | 1754·93 | 56985·9 | ${}^2D_2 - a\,{}^2F_3$ | 56984·9 |
| 1760·52 | sh w | | 56801·4 | | |
| 1764·67 | m | 1764·84 | 56667·8 | | |
| 1767·96 | m | | 56562·5 | | |
| 1769·68 | m | 1769·96 | 56507·4 | | |
| 1771·55 | sh w | 1771·80 | 56447·7 | $a\,{}^4F_3 - b\,{}^4P_3$ | 56455·0 |
| 1773·98 | ml | 1774·22 | 56370·4 | ${}^2D_3 - a\,{}^2\overline{G}_4$ | 56370·4 |
| 1775·94 | sh s | 1776·16 | 56308·2 | | |
| 1781·24 | sh w | | 56140·7 | | |
| 1782·71 | sh w | | 56094·4 | | |
| 1788·54 | l | | 55911·5 | ${}^2D_2 - a\,{}^2\overline{D}_3$ | 55911·6 |
| 1792·88 | sh w | 1793·04 | 55776·2 | $a\,{}^2\overline{F}_3 - b\,{}^4\overline{D}_4$ | 55781·8 |
| 1794·90 | sh | | 55713·4 | $a\,{}^2\overline{F}_3 - b\,{}^4\overline{D}_2$ | 55711·0 |
| 1804·47 | l | | 55417·9 | ${}^2D_3 - a\,{}^4F_4$ | 55416·7 |
| 1807·19 | sh | 1806·98 | 55334·5 | | |
| 1810·40 | sh | | 55236·4 | | |
| 1811·73 | sh s | | 55195·9 | | |
| 1819·29 | sh s | | 54966·5 | | |
| 1823·09 | m | | 54851·9 | | |
| 1829·96 | m | | 54646·0 | | |
| 1847·22 | m | 1847·47 | 54135·4 | | |
| 1849·30 | sh w | 1849·54 | 54074·5 | | |
| 1854·14 | m | 1854·16 | 53933·4 | | |
| 1858·73 | sh s | 1858·71 | 53800·2 | | |

line has the appearance of being double), the third the wave-length as given by Bloch,* the fourth the wave-number, the fifth the allocation of terms, if any, and the last column the wave-number calculated by adopting the values already given for $^2D_3$ and $^2D_2$.

*Wave-length Measurements in the Arc in Air.*

In order to continue the above observations into longer wave-lengths, where more reliance might be put upon the measurements, an arc was burned in air between pure nickel electrodes (from Adam Hilger, Ltd.). The arc was maintained by cells (110 volts) at 5 ampères. The exposures were made on Schumann plates with a Hilger quartz spectrograph (small size), having a dispersion of about 10 A.U. per millimetre in the region investigated.

Taking as standards three spark lines determined by Shenstone in the neighbourhood of 2000 A.U., the lines of wave-length below this were roughly determined. This allowed the allocation to two lines of the combinations $a\,^2\bar{F}_3 - b\,^4P_2$ and $a\,^2\bar{F}_4 - b\,^4P_3$, and their true values were calculated from Shenstone's term-scheme. These two lines (1938·59 and 1886·06 respectively) were then used with 2004·93 ($a\,^2D_3 - c\,^2P_2$) to calculate a new Hartmann formula, so that lines within the range of the formula might be more accurately calculated.

Wave-lengths were also measured in the same way on plates taken by fusing nickel wires in front of the slit of the spectrograph. In this way some lines were obtained which were either absent in the arc photographs or so very faint that measurement was impossible. In the Table II which follows the first column contains the wave-lengths measured as above (F after the wave-length means that the line has been measured in the fuse-spectrum only), the second the wave-number, the third the terms to which the line belongs, and the last column the calculated wave-number (assuming the values already used for $^2D_3$ and $^2D_2$). In the third column, Sh means that the line has been previously allocated to the terms by Shenstone.

*Other Evidence.*—It is believed that the values adopted for the D-terms are correct within one unit of wave-number.

These values imply a separation 1506·9. Now it is possible to form an estimate of what this separation should be, approximately, since these D terms will be the limits to which the arc triplet D terms tend. Consequently the overall separations of these D triplets in the arc spectrum will tend towards the D-separation in the spark spectrum. Fortunately the arc spectrum has

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* 'J. Phys. et Rad.,' vol. 6, p. 105 (1925).

Table II.

| Wave-length. | Wave-number. | Terms. | Wave-number (calculated). |
|---|---|---|---|
| 1965·35 | 50881·5 | $a\ ^4\overline{P}_3 - c\ ^2F_4$ (Sh) | 50881·5 |
| 1953·44 | 51191·7 | $a\ ^2D_3 - b\ ^4\overline{S}_2$ (Sh) | 51192·2 |
| 1951·94 F | 51231·1 | $^2D_2 - a\ ^4\overline{D}_3$ | 51230·5 |
| 1940·12 F | 51543·2 | | |
| 1939·60 F | 51557·0 | $^2D_3 - a\ ^4\overline{D}_4$ | 51556·9 |
| 1918·40 | 52126·8 | $^2D_2 - a\ ^4\overline{D}_2$ | 52127·0 |
| 1898·70 F | 52667·6 | $^2D_2 - a\ ^4\overline{D}_1$ | 52668·0 |
| 1897·62 F | 52697·6 | $a\ ^2F_3 - b\ ^2F_3$ | 52698·6 |
| 1896·18 | 52737·6 | $^2D_3 - a\ ^4D_3$ | 52737·4 |
| 1893·65 F | 52808·1 | $a\ ^2D_3 - c\ ^2F_4$ (Sh) | 52809·2 |
| 1881·28 F | 53155·3 | $a\ ^2F_3 - b\ ^2\overline{D}_2$ (Sh) | 53158·5 |
| 1860·76 F | 53741·5 | $a\ ^2F_3 - b\ ^2D_3$ | 53739·7 |
| 1858·68 F | 53801·6 | | |

been ordered into terms by Bechert and Sommer.* The triplet D-separations according to these workers are successively:—

$$\overline{d_3}^1 - \overline{d_1}^1 = 1508\cdot29$$

and

$$\overline{d_3}^2 - \overline{d_1}^2 = 1506\cdot29,$$

while the spark D-separation here found is

$$^2D_3 - {}^2D_2 = 1506\cdot9.$$

This constancy of separation parallels that of the $f$-terms, to which Shenstone† has drawn attention.

### *The Missing* S *and* P *Terms.*

While nothing has been found during the course of this work to determine these three missing terms with certainty, it is thought possible that these terms may be accounted for in this way. Majumdar‡ has investigated the nickel spectrum in the ultra-violet in the oven and in the under-water spark for reversals. Most of the reversals so found belong to the arc spectrum but a few undoubtedly are spark lines. Among the lines not allocated to the arc-terms are two lines, 2802·29 and 2794·83 A.U., having a wave-number difference of 95·2. Majumdar finds them reversed in both the oven and the under-water spark, so that they should belong to low-levels and be strong combinations.

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* 'Ann. Physik,' vol. 77, p. 351 (1925).

† *Loc. cit.*

‡ 'Z. Physik,' vol. 39, p. 562 (1926).

Yet they do not fit in with the low terms either of the arc or the spark. Also the second line is listed by Exner and Haschek* in the spark only. It is here suggested that these lines may be $^2S_1 - {}^2P_2$ and $^2S_1 - {}^2P_1$. Since none of the terms are known, this does not make it possible to determine any of the terms singly. But by making plausible estimates of the values of the terms it is possible to guess at other lines involving them. In this way the long line 1692·44 and the strong medium-length line 1652·83 suggest themselves as $^2D_2 - {}^2P_1$ and $^2D_3 - {}^2P_2$. This would mean that the missing terms were $^2P_1$, 52200; $^2P_2$, 52109; and $^2S_1$, 16432. The following allocations would then be possible:—

| Wave-length. | Wave-number. | Terms (?). | Wave-number (calculated). |
|---|---|---|---|
| 2802·278 H. | 35674·7 | $^2S_1 - {}^2P_2$ | — |
| 2794·83 Ma. | 35769·86 | $^2S_1 - {}^2P_1$ | — |
| 1692·44 M. | 59086·3 | $^2D_2 - {}^2P_1$ | — |
| 1652·83 M. | 60502·3 | $^2D_3 - {}^2P_2$ | — |
| 3170·735 H. | 31529·4 | $a\,{}^2\overline{P}_2 - {}^2P_1$ | 31523 |
| 3234·0 EH. | 30912·7 | $a\,{}^2\overline{P}_1 - {}^2P_2$ | 30910 |
| 2672·73 EH. | 37403·8 | $a\,{}^2D_3 - {}^2P_2$ | 37395 |
| 2791·01 EH. | 35818·8 | $a\,{}^4\overline{P}_2 - {}^2P_1$ | 35806 |
| 2802·278 H. | 35674·7 | $a\,{}^4\overline{P}_1 - {}^2P_2$ | 35667 |
| 2794·93 EH. | 35768·5 | $a\,{}^4\overline{P}_1 - {}^2P_1$ | 35758 |

(In the above the letters refer to the authority for the wave-length: H., Hamm,† Ma., Majumdar; M., Author; E.H., Exner and Haschek.)

If these suggestions are correct, then $^2S_1$ is very near to the low term $a\,{}^4\overline{P}_1$, and as it has the same $j$-value, all the lines having $^2S_1$ as the low-level term would lie close to the $a\,{}^4\overline{P}_1$ lines, and so perhaps escape notice.

Good agreement in the above is not to be expected, since the wave-lengths have been drawn from four different sources. The suggestion must, however, be regarded as highly speculative.

### *Standards in the Schumann Region.*

The determination of the D-terms above makes it possible to calculate the theoretical values of the wave-lengths from the last column of Table I. These can then be used as standard lines between which to interpolate the values of unknown lines.

Since the lines do not involve high terms, they are not very likely to be subject to fortuitous fluctuations in wave-length, and so are suitable lines for standards. Another advantage is that nickel is easily obtainable in the form of wire or rod.

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* Kayser's 'Handbuch der Spectroscopie.'

† 'Z. wiss. Photogr.,' vol. 13, p. 105 (1913).

For the convenience of readers a table of terms is here set out, being taken (with the exception of the low $^2D_{3,2}$ terms and the speculative low $^4S_1$ and middle $^2P_{2,1}$ terms) from Shenstone. In the last column, terms which should combine with the two ground terms are indicated by 2 and 3 for $^2D_2$ and $^2D_3$ respectively. The absence of a bracket to these numbers means that the lines corresponding have been found.

Table III.

| Term type. | Term value. | D combination. | Term type. | Term value. | D combination. |
|---|---|---|---|---|---|
| Low terms— | | | $a\ ^2F_3$ | 50098·9 | 2 3 |
| $^2D_3$ | – 8392·9 | | $a\ ^2\overline{D}_2$ | 50311·5 | 2 3 |
| $^2D_2$ | – 6886·0 | | $^2P_2$ ? | 52109 | (2) 3 |
| $a\ ^4\overline{F}_5$ | 0·0 | | $^2P_1$ ? | 52200 | 2 |
| $a\ ^4\overline{F}_4$ | 936·4 | | $b\ ^4P_3$ | 58176·8 | 2 3 |
| $a\ ^4\overline{F}_3$ | 1721·8 | | $b\ ^4P_2$ | 58185·4 | (2 3) |
| $a\ ^4\overline{F}_2$ | 2270·1 | | $b\ ^4P_1$ | 58636·6 | (2) |
| $a\ ^2\overline{F}_4$ | 5156·2 | | $b\ ^2F_3$ | 59300·1 | 2 (3) |
| $a\ ^2\overline{F}_3$ | 6601·5 | | $b\ ^2F_4$ | 59736·9 | 3 |
| $a\ ^2D_3$ | 14714·0 | | $b\ ^2\overline{D}_2$ | 59760·0 | 2 (3) |
| $a\ ^2D_2$ | 15402·0 | | $b\ ^2P_1$ | 59887·3 | (2) |
| $a\ ^4\overline{P}_3$ | 16394·0 | | $b\ ^2\overline{D}_3$ | 60341·2 | (2) 3 |
| $^4S_1$ ? | 16432 ? | | $b\ ^2P_2$ | 60571·4 | 2 3 |
| $a\ ^4\overline{P}_1$ | 16441·8 | | $b\ ^4\overline{D}_3$ | 62241·1 | 2 3 |
| $a\ ^4\overline{P}_2$ | 16641·7 | | $b\ ^4\overline{D}_2$ | 62312·5 | 2 (3) |
| $a\ ^2\overline{P}_2$ | 20676·5 | | $b\ ^4\overline{D}_1$ | 62354·4 | (2) |
| $a\ ^2\overline{P}_1$ | 21199·0 | | $b\ ^4D_4$ | 62383·3 | 3 |
| $a\ ^2G_5$ | 24105·3 | | $c\ ^2\overline{D}_3$ | 63376·8 | 2 3 |
| $a\ ^2G_4$ | 24129·3 | | $c\ ^2\overline{D}_2$ | 63981·0 | 2 (3) |
| | | | $c\ ^2P_2$ | 64591·1 | 2 3 |
| Middle terms— | | | $c\ ^2P_1$ | 65508·6 | 2 |
| $a\ ^4\overline{D}_4$ | 43164·0 | 3 | $c\ ^2\overline{S}_1$ | 65888·9 | 2 |
| $a\ ^4\overline{D}_3$ | 44344·5 | 2 3 | $b\ ^4\overline{S}_2$ | 65906·2 | (2 3) |
| $a\ ^4\overline{G}_5$ | 44971·1 | | $b\ ^2H_5$ | 66755·5 | |
| $a\ ^4\overline{G}_6$ | 45102·7 | | $b\ ^2H_6$ | 67327·5 | |
| $a\ ^4\overline{D}_2$ | 45241·0 | 2 (3) | $c\ ^2F_3$ | 67495·4 ? | (2 3) |
| $a\ ^4\overline{D}_1$ | 45782·0 | 2 | $c\ ^2F_4$ | 67523·2 ? | 3 |
| $a\ ^4\overline{G}_4$ | 45868·5 | (3) | $b\ ^2\overline{G}_4$ | 71428·6 | (3) |
| $a\ ^4F_5$ | 46163·2 | | $b\ ^2\overline{G}_5$ | 71529·7 | |
| $a\ ^4\overline{G}_3$ | 46624·7 | (2 3) | | | |
| $a\ ^2\overline{G}_5$ | 46905·9 | | High terms— | | |
| $a\ ^4F_4$ | 47023·8 | 3 | $d\ ^4\overline{F}_5$ | 83404·4 | |
| $a\ ^4F_3$ | 47681·1 | (2 3) | $d\ ^4\overline{F}_4$ | 83929·8 | |
| $a\ ^2\overline{G}_4$ | 47977·5 | 3 | $d\ ^4\overline{F}_3$ | 84993·9 | |
| $a\ ^4F_2$ | 48030·5 | (2 3) | $d\ ^4\overline{F}_2$ | 85671·0 | |
| $a\ ^2F_4$ | 48686·2 | 3 | $d\ ^2\overline{F}_4$ | 85132·2 | |
| $a\ ^2D_3$ | 49025·6 | 2 3 | $d\ ^2\overline{F}_3$ | 86333·0 | |

## *Note on the Spectra of* CU II *and* Ag II.

A. G. Shenstone* has recently published a term-scheme for Ag II, and in this paper he quotes the results of R. J. Lang, who has measured the lines involving the ground-term $^1S_0$ of Cu II in the interrupted arc *in vacuo*. The same lines were independently identified and measured by the author in the fuse (the second paper referred to above), and it is interesting to compare the values obtained. For convenience in comparison they are here set out :—

| | | | |
|---|---|---|---|
| Lang ............ | 1358·84 | 1368·00 | 1472·48 |
| Author .......... | 1358·76 | 1367·92 | 1472·38 |

In the same paper are quoted the measurements of H. E. White on the wave-lengths of the lines of silver involving the ground-term. The author had also prepared a term-scheme of Ag II, but as it agreed entirely with the scheme of Shenstone (although not so detailed) it was naturally shelved. It is thought worth while giving here the wave-lengths of the $^1S_0$ lines measured in the fuse, however, as confirmation of Mr. White's measurements :—

| | | | |
|---|---|---|---|
| White .......... | 1112·46 | 1107·05 | 1195·87 |
| Author .......... | 1112·35 | 1107·01 | 1195·76 |

These lines of copper and silver are reproduced in 1 and 2, Plate 6.

### DESCRIPTION OF PLATE 6.

(1) Fuse-spectrum of silver wire, 99·5 per cent. Ag., 20 gauge, showing the lines involving the ground-term $^1S_0$ (magnification $3\frac{1}{2}$).

(2) Fuse-spectrum of copper wire, 20 gauge, showing ground-term lines corresponding to the silver lines in (1) (magnification $3\frac{1}{2}$).

(3) Fuse-spectrum of nickel wire, commercial, 24 gauge, showing the lines involving the ground-terms $^2D_3$, $^2D_2$ (magnification 1·5).

(4) and (5) Further enlargement of (3) to show detail (magnification 5·6).

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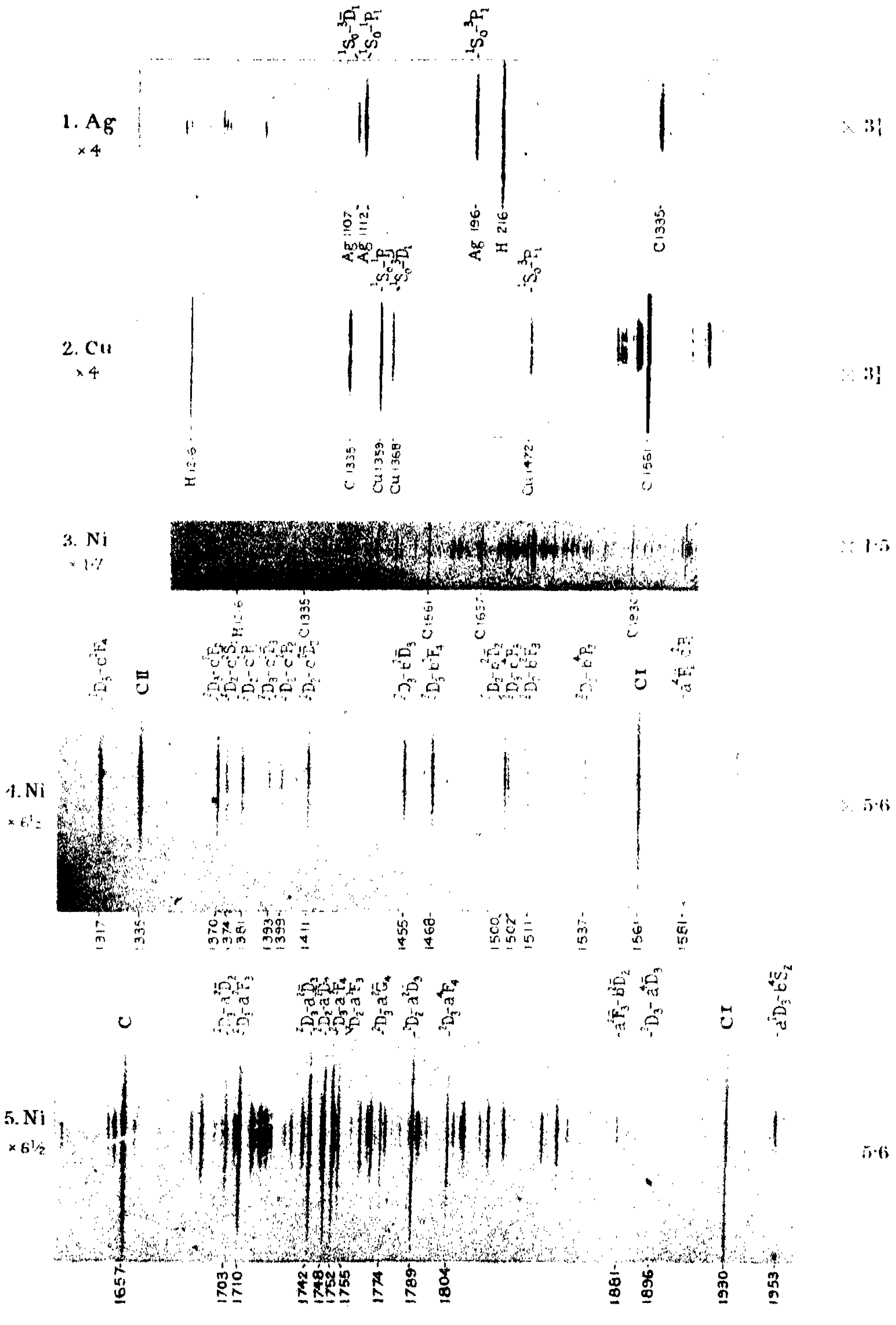
* 'Phys. Rev.,' vol. 31, p. 317 (1928).



The magnification given on the left is that of the original photograph: that on the right the actual magnification on this plate.

(*Facing p.* 142.)

## *Summary.*

The method of the fuse-spectrum devised by the author is particularly suited to the investigation of ground-terms, and is here applied to the elucidation of those belonging to Ni II.

Using the fuse horizontally in the vacuum grating spectrograph and very near the slit, there is a tendency to form " long and short lines " in spite of the astigmatic action of the grating. Many lines, obviously connected on account of their length and strength, were found on analysis to belong to the hitherto unknown ground-terms $^2D_3$ and $^2D_2$ of Ni II.

Since the combining middle terms are known with accuracy a determination of the values of $^2D_3$ and $^2D_2$ allows the calculation of conveniently spaced lines, which can be used as standards in the Schumann region. The lines extend from 1317 to 1940 A.U.

In a concluding note the lines involving the ground-terms of Cu II and Ag II, as measured by the author, are given for comparison with the measurements made by Lang and by White respectively.

[*Note added* 8 *November*, 1928.—In a private communication Prof. Shenstone tells me that the terms $^2D_{3,2}$ have been fixed by R. J. Lang at almost exactly the same values as determined here, but that he considers them fixed here with greater certainty.

Also the lines of Majumdar quoted in the paragraph " The Missing S and P Terms " are probably impunity lines, so that the missing S and P terms suggested here should be dismissed as spurious.]

# *The Spectrum of Doubly Ionised Fluorine (F III).*

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(Communicated by A. Fowler, F.R.S.—Received September 4, 1928.)

[Plate 7.]

## *Introductory.*

When discharges of gradually increasing intensity are passed through a vacuum tube containing silicon tetrafluoride ($SiF_4$), the lines attributable to fluorine appear successively in four fairly compact groups. Between the first three of these groups it is possible, by careful control of the conditions of discharge, to make a clear separation; the fourth, though distinguishable from the third, is less easily isolated. The first group has already been identified as the spectrum of the neutral atom of fluorine (F I).* It is probable, therefore, that the others are assignable to F II, F III, and F IV, respectively. The present paper contains an account of the third group, with a partial analysis. The resemblance between the spectrum and that of singly ionised oxygen ($O^+$), which has the same electron structure as doubly ionised fluorine, confirms its assignment to $F^{++}$.†

## *Experimental Arrangements.*

The lines of the spectrum in question appear when strongly condensed discharges are passed through silicon tetrafluoride at very low pressure. The intensity of discharge necessary is indicated by the fact that the lines do not appear in the photographs which accompany Prof. Fowler's study of the silicon spectra,‡ although Si III and Si IV are shown there in considerable strength. The method of preparation and purification of the gas has been described in the first paper on the spectrum F I (*loc. cit.*). With the stronger discharges, however, the lines of impurities arising from the material of the tube and electrodes were considerably increased in number, and great care was necessary to identify them as completely as possible. Boron, carbon, oxygen, sodium, magnesium and aluminium were the chief impurities found; in particular, the

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* 'Roy. Soc. Proc.,' A, vol. 113, p. 323 (1926); A, vol. 117, p. 407 (1928).

† It is convenient to confine the symbols F I, F II, F III, ... to spectra, and the symbols F, $F^+$, $F^{++}$ ... to the corresponding atoms.

‡ 'Phil. Trans.,' A, vol. 225, p. 1 (1925).

B III pair at λλ 2068, 2066 occurred in surprising strength, and formed the most intense lines in the spectrum. A few lines which have not been identified have been removed from the list of F III lines on account of their appearance in the spectrum, kindly lent by Prof. Fowler, of an "empty" tube containing the minimum amount of air necessary to permit the discharge to pass. The lines of silicon were identified by means of Fowler's tables.*

The spectra used for measurement purposes were obtained by means of three instruments—(1) a 10-ft. concave grating (first order); (2) a quartz Littrow spectrograph, giving a dispersion ranging from 5·5 A. per millimetre at λ 3100 to 2 A. per millimetre at λ 2300; and (3) a quartz spectrograph, having separate telescope and collimator, and giving an average dispersion of 8·4 A. per millimetre over the range λ 2800 to λ 2200. The wave-lengths adopted for the stronger lines above λ 2300 are the mean values obtained from several plates taken with the first two of these instruments; it is unlikely that they are in error by more than 0·01 A. They are given in Table I to the third decimal place. Lines below λ 2300, and the weaker lines throughout the whole range, were obtained only with the last-named instrument, and their wave-lengths are therefore less certain. The degree of accuracy with these lines varies with their intensity and position in the spectrum, but the error should not exceed 0·1 A. in the most unfavourable case, and is doubtless generally much less than this.

The lines were measured usually with reference to iron arc standards, but in some instances internal standards of silicon and other impurities were employed. As the spectrum appeared only when the pressure in the tube was very low, no displacement with pressure was observed, and the wave-lengths obtained from different plates were very consistent with one another. Among the plates measured was one taken several years ago at the Imperial College by Mr. J. S. Clark, in which the stronger lines of F III appeared with excellent definition.

### *The Lines of the F III Spectrum.*

Three hundred and fourteen lines belonging to the F III spectrum have been measured and are included in Table I. There are possibly some additional lines in the Schumann region among the lines of F IV, but until the latter spectrum has been analysed it is impossible to distinguish them with certainty. None of the lines in Table I has appeared in any previously published list of fluorine lines, except the 11 lines in the extreme ultra-violet, at the end of the table, which have been given by Millikan and Bowen, and are here copied from their lists.† The intensities are eye estimates, and necessarily suffer in precision from the variation of sensitivity of the photographic plates over the region covered by the spectrum. The letters which occasionally accompany the intensity indices have their usual meanings.

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* *Loc. cit.*

Table I.—Lines of Doubly Ionised Fluorine (F III).

| λ (Int.). | ν. | Combinations. | | Remarks. |
|---|---|---|---|---|
| | | Quartet. | Doublet. | |
| 3267·202 (4) | 30598·43 | | | |
| 64·162 (9) | 626·93 | | | |
| 54·837 (2) | 714·68 | | | |
| 53·79 (½) | 724·5 | | | |
| 53·43 (2½) | 728·0 | | | |
| 52·96 (½) | 732·4 | | | |
| 38·51 (1) | 869·5 | | | |
| 13·972 (6) | 31105·19 | | $3s$ $P_2$ — $3p$ $D_2$ | |
| 01·19 (2) | 229·4 | | | |
| 3194·66 (1) | 293 2 | | | |
| 94·21 (1) | 297·6 | | | |
| 92·27 (½) | 316·7 | | | |
| 91·45 (2) | 324·7 | | | |
| 74·725 (10) | 489·71 | | $3s$ $P_1$ — $3p$ $D_2$ | |
| 74·125 (12) | 495·66 | | $3s$ $P_2$ — $3p$ $D_3$ | |
| *65·864 | 577·85 | $3s$ $P_3$ — $3p$ $D_2$ | | |
| 63·24 (1) | 604·4 | | | |
| 54·387 (4) | 692·74 | | | |
| 46·962 (8) | 767·51 | $3s$ $P_3$ — $3p$ $D_3$ | | |
| 45·536 (4) | 781·91 | $3s$ $P_2$ — $3p$ $D_1$ | | |
| 42·777 (3) | 809·81 | | | |
| 39·66 (½) | 841·4 | | | |
| 38·34 (2) | 854·8 | | | |
| 34·73 (1) | 891·4 | | | |
| 34·208 (8) | 896·77 | $3s$ $P_2$ — $3p$ $D_2$ | | |
| 32·769 (2) | 911·42 | | | |
| 29·34 (1) | 946·4 | | | |
| 25·69 (½) | 983·7 | | | |
| 25·14 (½) | 989·3 | | | |
| 24·762 (8) | 993·19 | $3s$ $P_1$ — $3p$ $D_1$ | | |
| 24·18 (3) | 999·2 | | | |
| 21·515 (12) | 32026·48 | $3s$ $P_3$ — $3p$ $D_4$ | | |
| 20·09 (2*n*) | 041·1 | | | Associated group; possibly F II. |
| 18·66 (1½*n*) | 055·8 | | | |
| 17·72 (1*n*) | 065·5 | | | |
| 15·669 (10) | 086·56 | $3s$ $P_2$ — $3p$ $D_3$ | | |
| 13·579 (8) | 108·10 | $3s$ $P_1$ — $3p$ $D_2$ | | |
| 3082·19 (½) | 435·1 | | | |
| 77·46 (1) | 484·9 | | | |
| 71·24 (1*n*) | 550·7 | | | ? C IV. |
| 68·19 (1) | 583·1 | | | |
| 66·71 (2) | 598·8 | $3p$ $S_2$ — $3d$ $D_3$ | | |
| 59·24 (2) | 678·4 | | | |
| 49·139 (8) | 786·64 | | | |

* Calculated value; line masked by strong Si line, λ 3165·72.

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† 'Phys. Rev.,' vol. 23, p. 11 (1924); 'Phil. Mag.,' p. 261 (Aug. 1924); 'Phys. Rev.,' vol. 29, p. 231 (1927).

Table I.—Lines of Doubly Ionised Fluorine (F III)—(continued).

| λ (Int.). | ν. | Combinations. | | Remarks. |
|---|---|---|---|---|
| | | Quartet. | Doublet. | |
| 3048·80 (2) | 32790·3 | | | |
| 47·077 (4) | 808·82 | | | |
| 42·808 (10) | 854·85 | | | |
| 39·746 (6) | 887·94 | | | |
| 39·254 (7) | 893·26 | | | |
| 35·40 (2) | 935·0 | | | |
| 34·54 (1½) | 944·3 | | | ? Impurity. |
| 32·68 (1) | 964·6 | | | |
| 03·15 (2) | 33288·7 | | | |
| 01·920 (3) | 302·33 | | | |
| 00·097 (4) | 322·57 | | | |
| 2999·465 (6) | 329·59 | | | |
| 97·513 (6) | 351·28 | | | |
| 97·168 (6) | 355·14 | $3p\ S_2 - 3d\ P_3$ | | |
| 94·273 (8) | 387·37 | | | |
| 92·3 (½) | 409·0 | | | |
| 88·45 (4*r*) | 452·5 | | | |
| 84·479 (5) | 496·94 | $3p\ S_2 - 3d\ P_2$ | | |
| 83·765 (4) | 504·96 | | | |
| 82·13 (1½) | 523·3 | | | |
| 78·145 (4) | 568·17 | $3p\ S_2 - 3d\ P_1$ | | |
| 66·89 (1) | 695·5 | | | |
| 61·596 (5) | 755·74 | | | |
| 59·666 (2+) | 777·76 | | | |
| 55·13 (2) | 829·6 | | | |
| 49·91 (1½) | 889·5 | | | |
| 47·26 (1) | 919·9 | | | |
| 32·479 (8) | 34090·89 | $3s\ P_3 - 3p\ P_2$ | | |
| 20·887 (4) | 226·18 | | | |
| 20·538 (6) | 230·27 | | | |
| 16·335 (10) | 279·60 | $3s\ P_3 - 3p\ P_3$ | | |
| 13·279 (8) | 315·56 | $3s\ P_2 - 3p\ P_1$ | | |
| 05·301 (6) | 409·78 | $3s\ P_2 - 3p\ P_2$ | | |
| 2899·75 (2) | 475·7 | | | |
| 95·458 (4) | 526·75 | $3s\ P_1 - 3p\ P_1$ | | |
| 94·32 (1) | 540·3 | | | |
| 92·94 (1½) | 556·8 | | | |
| 89·447 (8) | 598·58 | $3s\ P_2 - 3p\ P_3$ | | |
| 87·559 (8) | 621·19 | $3s\ P_1 - 3p\ P_2$ | | |
| 76·49 (3) | 754·5 | | | *a* Lines marked *a* are very diffuse and shaded towards red on one plate; they possibly belong to F II. |
| 75·87 (3) | 761·9 | | | |
| 74·81 (5) | 774·7 | | | *a* |
| 73·63 (2) | 789·0 | | | |
| 73·12 (4) | 795·2 | | | |
| 71·40 (8) | 816·0 | | | *a* |
| 69·993 (3) | 833·09 | | $3p\ P_2 - 3d\ D_2$ | |
| 67·30 (5) | 865·8 | | | *a* |
| 65·670 (4) | 885·64 | | $3p\ D_3 - 3d\ F_3$ | |
| 62·866 (6) | 919·80 | | $3p\ P_1 - 3d\ D_2$ | |
| 60·308 (9) | 951·02 | | $3p\ P_2 - 3d\ D_3$ | |
| 41·7 (3) | 35180·3 | | | |
| 39·52 (0) | 206·9 | | | ? Impurity. |
| 35·606 (9) | 255·49 | | $3p\ D_3 - 3d\ F_4$ | |
| 33·962 (8) | 275·94 | | $3p\ D_2 - 3d\ F_3$ | |
| 26·081 (5) | 374·31 | | | |
| 23·77 (3) | 403·2 | | | |

Table I.—*Lines of Doubly Ionised Fluorine (F III)*—(*continued*).

| λ (Int.). | ν. | Combinations. |  | Remarks. |
|---|---|---|---|---|
|  |  | Quartet. | Doublet. |  |
| 2820·695 (4) | 35441·84 |  |  |  |
| 18·302 (5) | 471·94 |  | $3s\ \mathrm{P}_2 - 3p\ \mathrm{P}_1$ |  |
| 11·422 (10) | 558·74 |  | $3s\ \mathrm{P}_2 - 3p\ \mathrm{P}_2$ |  |
| 07·5 (0) | 608·4 |  |  |  |
| 06·0 (½) | 627·4 |  |  |  |
| 04·0 (½) | 652·9 |  |  |  |
| 00·0 (0) | 703·8 |  |  |  |
| 2797·9 (1) | 730·6 |  |  |  |
| 96·7 (½) | 745·9 |  |  |  |
| 95·500 (4) | 761·26 |  |  | Probably impurity. |
| 94·2 (3) | 777·9 |  |  |  |
| 93·18 (2) | 790·96 |  |  |  |
| 90·6 (0) | 824·0 |  |  |  |
| 89·352 (3) | 840·07 |  |  | ? C IV. |
| 88·093 (6) | 856·26 |  | $3s\ \mathrm{P}_1 - 3p\ \mathrm{P}_1$ |  |
| 85·9 (2) | 884·5 |  |  |  |
| 81·956 (4) | 935·35 |  |  |  |
| 81·350 (5) | 943·18 |  | $3s\ \mathrm{P}_1 - 3p\ \mathrm{P}_2$ |  |
| 78·7 (½*n*) | 977·5 |  |  |  |
| 77·0 (½) | 999·5 |  |  |  |
| 59·81 (3) | 36223·7 |  |  |  |
| 59·589 (10) | 226·60 |  |  |  |
| 56·664 (5) | 265·02 |  |  |  |
| 55·556 (7) | 279·61 |  |  |  |
| 55·307 (4) | 282·89 |  |  |  |
| 52·8 (½) | 315·9 |  |  |  |
| 51·8 (1) | 329·1 |  |  |  |
| 47·870 (5) | 381·08 |  |  |  |
| 44·5 (½) | 425·8 |  |  |  |
| 40·3 (1) | 481·6 |  |  |  |
| 39·2 (1—) | 496·2 |  |  |  |
| 37·954 (4) | 512·84 |  | $3s\ \mathrm{P}_2 - 3p\ \mathrm{S}_1$ |  |
| 33·8 (½) | 568·3 |  |  |  |
| 33·1 (½*n*) | 577·7 |  |  |  |
| 32·6 (0) | 584·4 |  |  |  |
| 29·0 (1*n*) | 632·6 |  |  |  |
| 27·93 (2) | 646·9 |  |  |  |
| 25·82 (2*n*) | 675·4 |  |  |  |
| 22·1 (0) | 725·5 |  |  |  |
| 20·0 (1½) | 753·8 |  |  |  |
| 18·2 (2) | 778·2 |  |  |  |
| 17·1 (½) | 793·1 |  |  |  |
| 09·408 (3) | 897·51 |  | $3s\ \mathrm{P}_1 - 3p\ \mathrm{S}_1$ |  |
| 06·6 (½) | 935·8 |  |  |  |
| 04·7 (0) | 961·7 |  |  |  |
| 2695·45 (4) | 37088·5 |  |  | ? O III. |
| 94·9 (0) | 096·1 |  |  |  |
| 94·0 (½) | 108·5 |  |  |  |
| 92·790 (5) | 125·2 |  |  |  |
| 86·8 (½) | 208·0 |  |  |  |
| 82·44 (1) | 268·4 |  |  | } ? Impurities. |
| 78·40 (1) | 324·7 |  |  |  |
| 77·5 (1+) | 337·2 |  |  |  |
| 68·71 (2) | 460·1 |  |  |  |
| 68·18 (2) | 467·6 |  |  |  |
| 64·390 (4) | 520·90 |  |  |  |

Table I.—Lines of Doubly Ionised Fluorine (F III)—(continued).

| λ (Int.). | ν. | Combinations. | | Remarks. |
|---|---|---|---|---|
| | | Quartet. | Doublet. | |
| 2656·475 (6) | 37632·69 | Probable multiplet, discussed in paper | | |
| 56·294 (3) | 635·25 | | | |
| 53·757 (5) | 671·23 | | | |
| 53·491 (4) | 675·00 | | | |
| 53·252 (2) | 678·40 | | | |
| 51·958 (3) | 696·78 | | | |
| 51·723 (3+) | 700·12 | | | |
| 51·550 (3) | 702·58 | | | |
| 50·5 (½*n*) | 717·5 | | | ? Double. |
| 48·4 (0) | 747·4 | | | |
| 47·4 (0) | 761·7 | | | |
| 45·5 (0) | 788·8 | | | |
| 41·3 (2) | 848·9 | | | |
| 39·60 (2) | 873·2 | | | |
| 39·45 (3) | 875·3 | | | |
| 39·05 (4) | 881·1 | | | |
| 35·33 (2) | 934·6 | | | |
| 34·8 (½*n*) | 942·2 | | | |
| 30·93 (1) | 998·1 | | | ? Impurity. |
| 29·686 (8) | 38016·03 | | | |
| 27·2 (1*n*) | 052·0 | | | |
| 25·000 (7) | 083·89 | | | |
| 23·8 (½) | 101·3 | $3p\ D_4 - 3d\ F_3$ | | |
| 17·3 (1) | 195·9 | | | |
| 13·5 (½) | 251·5 | $3p\ D_3 - 3d\ F_2$ | | |
| 13·083 (5) | 257·56 | $3p\ D_4 - 3d\ F_4$ | | |
| 10·8 (½+) | 291·0 | | | |
| 06·045 (5) | 360·87 | $3p\ D_3 - 3d\ F_3$ | | |
| 02·9 (0) | 407·2 | | | |
| 00·551 (4) | 441·91 | $3p\ D_2 - 3d\ F_2$ | | |
| 2599·7 (2) | 454·5 | | | |
| 99·230 (8) | 461·45 | $3p\ D_4 - 3d\ F_5$ | | |
| 96·5 (1) | 501·9 | | | |
| 95·488 (7) | 516·90 | $3p\ D_3 - 3d\ F_4$ | | |
| 93·88 (1) | 540·7 | | | |
| 93·195 (6) | 550·95 | $3p\ D_2 - 3d\ F_3$ | | |
| 92·804 (6−) | 556·76 | $3p\ D_1 - 3d\ F_2$ | | |
| 92·65 (1) | 559·0 | $3p\ P_3 - 3d\ D_3$ | | |
| 92·43 (1) | 562·3 | $3p\ P_3 - 3d\ D_2$ | | |
| 83·760 (7) | 691·71 | $3p\ P_3 - 3d\ D_4$ | | |
| 80·031 (6) | 747·63 | $3p\ P_2 - 3d\ D_3$ | | |
| 79·846 (8) | 750·41 | $3p\ P_2 - 3d\ D_2$ | | |
| 77·19 (2) | 790·4 | $3p\ P_2 - 3d\ D_1$ | | |
| 73·596 (4) | 844·51 | $3p\ P_1 - 3d\ D_2$ | | |
| 70·917 (4−) | 884·99 | $3p\ P_1 - 3d\ D_1$ | | |
| 70·2 (½) | 895·8 | | $3p\ D_3 - 3d\ D_2$ | |
| 69·4 (0) | 907·9 | | | |
| 64·83 (1*n*) | 977·3 | | | |
| 62·413 (4) | 39014·03 | | $3p\ D_3 - 3d\ D_3$ | |
| 54·5 (½) | 134·9 | | | |
| 53·3 (½) | 153·3 | | | |
| 52·2 (1) | 170·1 | | | |
| 50·80 (2) | 191·6 | | | |
| 50·04 (1) | 203·3 | | | Cl 2550·02 (5) (Angerer). |
| 49·87 (1½) | 205·9 | | | |
| 49·63 (3) | 209·6 | | | |
| 47·8 (½) | 237·8 | | | |
| 44·63 (4) | 286·6 | | $3p\ D_2 - 3d\ D_2$ | |

Table I.—Lines of Doubly Ionised Fluorine (F III)—(continued).

| λ (Int.). | ν. | Combinations. | | Remarks. |
|---|---|---|---|---|
| | | Quartet. | Doublet. | |
| 2543·4 (1) | 39305·7 | | | |
| 42·767 (6) | 315·45 | $3p\ \mathrm{P}_3 - 3d\ \mathrm{P}_3$ | | |
| 41·0 (½) | 342·8 | | | |
| 40·3 (1) | 353·6 | | | |
| 37·06 (½) | 403·8 | | $3p\ \mathrm{D}_2 - 3d\ \mathrm{D}_3$ | |
| 33·644 (4) | 456·99 | $3p\ \mathrm{P}_3 - 3d\ \mathrm{P}_2$ | | |
| 30·66 (2) | 503·6 | $3p\ \mathrm{P}_2 - 3d\ \mathrm{P}_3$ | | |
| 29·9 (0) | 515·4 | | | ? C IV. |
| 22·5 (0) | 631·3 | | | |
| 21·590 (4) | 645·59 | $3p\ \mathrm{P}_2 - 3d\ \mathrm{P}_2$ | | |
| 17·07 (3) | 716·9 | $3p\ \mathrm{P}_2 - 3d\ \mathrm{P}_1$ | | |
| 15·62 (4) | 739·7 | $3p\ \mathrm{P}_1 - 3d\ \mathrm{P}_2$ | | |
| 11·16 (1) | 810·3 | $3p\ \mathrm{P}_1 - 3d\ \mathrm{P}_1$ | | |
| 05·3 (0) | 903·4 | | | |
| 03·6 (½+) | 930·5 | | | |
| 2497·72 (2) | 40024·5 | | | |
| 96·79 (1) | 039·4 | | | |
| 95·57 (½*n*) | 058·9 | | | |
| 93·78 (½) | 087·7 | | | } ? Impurities. |
| 92·09 (½+) | 098·8 | | | |
| 92·58 (0) | 107·0 | | | |
| 91·98 (0+) | 116·6 | | | |
| 85·82 (½) | 216·0 | | | |
| 84·360 (9) | 239·67 | $3s\ \mathrm{P}_3 - 3p\ \mathrm{S}_2$ | | |
| 83·01 (0) | 261·7 | | | |
| 80·63 (½*n*) | 300·2 | | | |
| 79·78 (½) | 314·0 | | | |
| 78·709 (6) | 331·40 | | | |
| 78·08 (½) | 341·6 | | | |
| 75·45 (½*n*) | 384·5 | | | |
| 74·2 (0*n*) | 404·4 | | | |
| 70·48 (2) | 465·8 | | | |
| 70·279 (7) | 469·02 | | | |
| 66·162 (4) | 536·60 | | | |
| 64·834 (8) | 558·41 | $3s\ \mathrm{P}_2 - 3p\ \mathrm{S}_2$ | | |
| 63·75 (2) | 576·3 | | | |
| 62·5 (2*n*) | 597·5 | | | |
| 58·7 (0*n*) | 659·6 | | | |
| 56·898 (5) | 689·41 | | | |
| 55·81 (½) | 707·4 | | | |
| 54·62 (1) | 727·2 | | | ? Impurity. |
| 52·070 (7) | 769·52 | $3s\ \mathrm{P}_1 - 3p\ \mathrm{S}_2$ | | |
| 51·56 (4) | 778·0 | | | |
| *49·5 (<5) | 811·5 | $3p\ \mathrm{D}_4 - 3d\ \mathrm{D}_3$ | | |
| 45·55 (2) | 878·2 | | | ? O II. |
| 41·622 (8) | 943·96 | $3p\ \mathrm{D}_4 - 3d\ \mathrm{D}_4$ | | |
| 36·31 (½) | 41033·2 | | | |
| 35·70 (1) | 043·5 | | | |
| 34·13 (6) | 069·9 | $3p\ \mathrm{D}_3 - 3d\ \mathrm{D}_3$ | | |
| 33·95 (3) | 072·9 | $3p\ \mathrm{D}_3 - 3d\ \mathrm{D}_2$ | | |
| 29·30 (½) | 151·6 | | | |
| 28·46 (1) | 165·9 | | | |
| 26·280 (4) | 202·84 | $3p\ \mathrm{D}_3 - 3d\ \mathrm{D}_4$ | | |
| 22·91 (3) | 260·1 | $3p\ \mathrm{D}_2 - 3d\ \mathrm{D}_3$ | | |
| 22·78 (4) | 262·4 | $3p\ \mathrm{D}_2 - 3d\ \mathrm{D}_2$ | | |
| 21·6 (0) | 281·8 | | | |

* Wave-length and intensity uncertain; line inseparable from Si line given by Fowler as λ 2449·53 (2*n*).

Table I.—Lines of Doubly Ionised Fluorine (F III)—(continued).

| λ (Int.). | ν. | Combinations. |  | Remarks. |
|---|---|---|---|---|
|  |  | Quartet. | Doublet. |  |
| 2420·44 (3) | 41302·3 | $3p\,D_3 - 3d\,D_1$ |  |  |
| 19·36 (½) | 320·7 |  |  |  |
| 18·44 (½) | 336·4 |  |  |  |
| 16·05 (4) | 377·3 | $3p\,D_1 - 3d\,D_2$ |  |  |
| 13·69 (3) | 417·7 | $3p\,D_1 - 3d\,D_1$ |  |  |
| 05·01 (4) | 567·1 | $3p\,D_4 - 3d\,P_3$ |  |  |
| 03·1 (0) | 600·9 |  |  |  |
| 2390·46 (2) | 820·2 |  |  | ? O III. |
| 81·99 (2*n*) | 968·9 | $3p\,D_3 - 3d\,P_2$ |  |  |
| 70·1 (0) | 42179·8 |  |  |  |
| 67·2 (1) | 231·1 | $3p\,D_2 - 3d\,P_1$ |  |  |
| 66·86 (2*n*) | 237·2 |  |  |  |
| 62·3 (0) | 318·1 |  |  |  |
| 52·4 (0) | 496·4 |  |  |  |
| 49·45 (½) | 550·1 |  |  |  |
| 36·7 (0) | 781·7 |  |  |  |
| 34·99 (½) | 813·6 |  |  |  |
| 34·12 (1) | 829·5 |  |  |  |
| 33·78 (2) | 835·8 |  |  |  |
| 29·93 (½) | 906·6 |  |  |  |
| 11·83 (2) | 43242·5 |  |  |  |
| 03·6 (0) | 396·9 |  |  |  |
| 00·27 (½) | 459·8 |  |  |  |
| 2299·74 (1½) | 469·8 |  |  |  |
| 98·31 (3) | 496·8 |  |  |  |
| 97·87 (1) | 505·1 |  |  |  |
| 95·50 (½) | 550·1 |  |  |  |
| 94·31 (1½*n*) | 572·6 |  |  |  |
| 90·9 (0) | 637·5 |  |  |  |
| 85·32 (1) | 744·0 |  |  |  |
| 84·0 (0) | 768·9 |  |  |  |
| 83·4 (0) | 780·6 |  |  |  |
| 80·83 (½) | 830·1 |  |  |  |
| 79·36 (3) | 858·3 |  |  |  |
| 75·80 (½) | 927·0 |  |  |  |
| 74·60 (1*n*) | 950·2 |  |  |  |
| 74·19 (½) | 958·1 |  |  |  |
| 73·75 (1) | 966·6 |  |  |  |
| 72·04 (2) | 999·7 |  |  |  |
| 68·7 (0) | 44065·0 |  |  |  |
| 52·83 (2) | 374·8 |  |  |  |
| 29·33 (1) | 842·5 |  |  |  |
| 17·34 (5) | 45085·0 |  | $3p\,S_1 - 3d\,P_2$ |  |
| 06·94 (3) | 297·4 |  | $3p\,S_1 - 3d\,P_1$ |  |
| 1049·6 | 95271 |  | $2p'\,P - 3pP$ | * |
| 658·34 (8) | 151897 | $2pS_2 - 2p'\,P_3$ |  |  |
| 657·69 | 2047 |  | $2p'\,D - 3pP$ |  |
| 656·86 (8) | 2239 | $2pS_2 - 2p'\,P_2$ |  |  |
| 656·10 (7) | 2416 | $2pS_2 - 2p'\,P_1$ |  |  |
| 630·17 (4) | 8687 |  | $2pP - 2p'\,D$ |  |
| 567·70 (7) | 176149 |  | $2pD - 2p'\,D$ |  |
| 465·08 (2) | 215017 |  | $2pP - 2p'\,P_2$ |  |
| 464·25 (2) | 5401 |  | $2pP - 2p'\,P_1$ |  |
| 430·15 (4) | 232477 |  | $2pD - 2p'P_2$ |  |
| 429·49 (2) | 2834 |  | $2pD - 2p'\,P_1$ |  |

* Wave-lengths and intensities copied from Millikan and Bowen's lists; the classifications, except those of λλ 1049·6, 657·69, are due to Bowen.

### *Theoretical Structure of the Spectrum.*

According to the Heisenberg-Hund theory, the spectrum of doubly ionised fluorine should be similar in structure to that of singly ionised oxygen, which has already been elucidated with a considerable degree of completeness.* The most prominent terms to be expected may be represented in the usual way by the following table. (The notation of terms is the same as that used in the second paper on F I (*loc. cit.*).)

Table II.—Predicted Terms of F III.

| Electrons outside rare gas shell. | Terms. | | | | |
|---|---|---|---|---|---|
| | Adopted prefix. | Term symbol. | | | |
| $2s^2 . 2p^3$ | $2p$ | $^4S$ | | $^2D$ | $^2P$ |
| $2s . 2p^4$ | $2p'$ | $^4P$ | $^2P$ | $^2D$ | $^2S$ |
| | | Core in $^3P$ state. | | Core in $^1D$ state. | Core in $^1S$ state. |
| $2s^2 . 2p^2 . 3s$ | $3s$ | $^4P$ | $^2P$ | $^2D$ | $^2S$ |
| $2s^2 . 2p^2 . 3p$ | $3p$ | $^4D$ $^4P$ $^4S$ | $^2D$ $^2P$ $^2S$ | $^2F$ $^2D$ $^2P$ | $^2P$ |
| $2s^2 . 2p^2 . 3d$ | $3d$ | $^4F$ $^4D$ $^4P$ | $^2F$ $^2D$ $^2P$ | $^2G$ $^2F$ $^2D$ $^2P$ $^2S$ | $^2D$ |
| $2s^2 . 2p^2 . 4s$ | $4s$ | $^4P$ | $^2P$ | $^2D$ | $^2S$ |
| $2s^2 . 2p^2 . 4p$ | $4p$ | $^4D$ $^4P$ $^4S$ | $^2D$ $^2P$ $^2S$ | $^2F$ $^2D$ $^2P$ | $^2P$ |
| $2s^2 . 2p^2 . 4d$ | $4d$ | $^4F$ $^4D$ $^4P$ | $^2F$ $^2D$ $^2P$ | $^2G$ $^2F$ $^2D$ $^2P$ $^2S$ | $^2D$ |
| $2s^2 . 2p^2 . 4f$ | $4f$ | $^4G$ $^4F$ $^4D$ | $^2G$ $^2F$ $^2D$ | $^2H$ $^2G$ $^2F$ $^2D$ $^2P$ | $^2F$ |
| $2s^2 . 2p^2 . 5s$ | $5s$ | $^4P$ | $^2P$ | $^2D$ | $^2S$ |

All the terms in the first two rows, except $2p'$ $^2S$, have already been recognised by Bowen† as giving rise to combinations in the extreme ultra-violet. A consideration of the probable magnitudes of the various terms shows that none of them would be expected to be involved in lines above λ 1200, which is the lowest wave-length at present attainable in closed vacuum-tube observations. So far as the present observations are concerned, therefore, the spectrum may be regarded as beginning with the $3s$ terms in the third row.

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* A. Fowler, 'Roy. Soc. Proc.,' A, vol. 110, p. 476 (1926); R. H. Fowler and Hartree, 'Roy. Soc. Proc.,' A, vol. 111, p. 83 (1926); Russell, 'Phys. Rev.,' vol. 31, p. 27 (1928).

† 'Phys. Rev.,' vol. 29, p. 231 (1927).

## *Analysis of the Spectrum.*

All the terms arising from the addition of a $3s$, $3p$ or $3d$ electron to a core in the $^3P$ state have been detected. The multiplets in which they occur are set out in Tables III and IV. They comprise 80 lines. For convenience, Bowen's multiplets in the extreme ultra-violet are also included in the tables, as well as two additional classifications in that region, which will be explained later.

Since no extended series of lines have been found, it has not been possible to assign accurate values to the terms, but it is nevertheless probable that the values adopted are not far from the true ones. They have been chosen in the following manner: It is easily deduced from the irregular doublet law that the ionisation potentials of atoms having the same number of external electrons but consecutive values of the nuclear charge should form an arithmetical progression with a common difference of approximately 6·9. In several cases in which this requirement can be tested, it is found to hold closely. Considering, therefore, the atoms, N, $O^+$, $F^{++}$, and adopting the respective values, 14·5† and 35·0‡ for the ionisation potentials of N and $O^+$, we arrive at 62·4 as the ionisation potential of $F^{++}$, corresponding to a value, 506,000, for the ground-term, $2p\ ^4S_2$. From Bowen's observations the values of $2p'\ ^4P_{321}$ follow immediately. The remaining quartet terms have been evaluated by a comparison of effective quantum numbers with those of O II. In the latter spectrum, the effective quantum numbers ($n^*$) of the terms $2p\ ^4S_2$ and $3p\ ^4S_2$ are respectively 1·245 and 2·488, giving a difference of 1·243. Assuming the same difference to hold for F III, and observing that $n^*$ for the adopted value of $2p\ ^4S_2$ is 1·397, we obtain a value 2·640 for $3p\ ^4S_2$, corresponding to a term value, 141,633. Adopting this figure, the magnitudes of the remaining quartet terms are found from observed lines.

No intercombinations between the doublet and quartet terms have been detected, and the process has therefore been applied independently to the doublet system. Here, however, since the N I spectrum is not sufficiently known for the irregular doublet law to be employed, a provisional start was made by assuming that the ratio of the $3d\ ^2F$ terms in the spectra O II and F III is the same as that of the $3d\ ^4F$ terms. The value 108250·0 was thus obtained for $3d\ ^2F_4$, and the observations then gave the magnitudes of the other doublet terms, with the exception of those involved in Bowen's lines. These were evaluated by using the effective quantum numbers, as already

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† Hopfield, 'Phys. Rev.,' vol. 26, p. 801 (1926).

‡ Russell, *loc. cit.*

## Table III.—Quartet Combinations.

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 151897 (8)* | 2p′ $^4P_3$ = 354103 | | | | | | | | | | | | | |
| −*342* | −*342* | | | | | | | | | | | | | |
| 152239 (8)* | $^4P_2$ = 353761 | | | | | | | | | | | | | |
| −*177* | −*177* | | | | | | | | | | | | | |
| 152416 (7)* | $^4P_1$ = 353584 | | | | | | | | | | | | | |
| | 3s $^4P_3$ = 181872·48 | 32026·48 (12) | *258·97* | 31767·51 (8) | *189·66* | 31577·85† | | | 34279·60 (10) | *188·71* | 34090·89 (8) | | | 40239·67 (9) |
| | *318·94* | | | *319·05* | | *318·92* | | | *318·98* | | *318·89* | | | *318·74* |
| | $^4P_2$ = 182191·42 | | | 32086·56 (10) | *189·79* | 31896·77 (8) | *114·86* | 31781·91 (4) | 34598·58 (8) | *188·80* | 34409·78 (6) | *94·22* | 34315·56 (8) | 40558·41 (8) |
| | *211·28* | | | | | *211·33* | | *211·18* | | | *211·41* | | *211·19* | *211·11* |
| | $^4P_1$ = 182402·70 | | | | | 32108·10 (8) | *114·91* | 31993·19 (8) | | | 34621·19 (8) | *94·44* | 34526·75 (4) | 40769·32 (7) |
| 2p $^4S_2$<br>506000 | | 3p $^4D_4$<br>149845·98 | *258·94* | $^4D_3$<br>150104·92 | *189·71* | $^4D_2$<br>150294·63 | *114·88* | $^4D_1$<br>150409·51 | 3p $^4P_3$<br>147592·87 | *188·71* | $^4P_2$<br>147781·58 | *94·32* | $^4P_1$<br>147875·90 | 3p $^4S_2$<br>141633·00 |
| | 3d $^4F_5$ = 111384·58 | 38461·45 (8) | | | | | | | | | | | | |
| | *203·69* | *203·89* | | | | | | | | | | | | |
| | $^4F_4$ = 111588·22 | 38257·56 (5) | *259·34* | 38516·90 (7) | | | | | | | | | | |
| | *155·64* | *156·3* | | *156·03* | | | | | | | | | | |
| | $^4F_3$ = 111743·86 | 38101·3 (½) | *259·6* | 38360·87 (5) | *190·08* | 38550·95 (6) | | | | | | | | |
| | *108·88* | | | *109·4* | | *109·04* | | | | | | | | |
| | $^4F_2$ = 111852·74 | | | 38251·5 (½) | *190·4* | 38441·91 (4) | *114·85* | 38556·76 (6−) | | | | | | |
| | 3d $^4D_4$ = 108901·60 | 40943·96 (8) | *258·88* | 41202·84 (4) | | | | | 38691·71 (7) | | | | | |
| | *132·7* | *132·5* | | *132·9* | | | | | *132·7* | | | | | |
| | $^4D_3$ = 109034·3 | 40811·5 (<5)† | *258·4* | 41069·9 (6) | *190·2* | 41260·1 (3) | | | 38559·0 (1) | *188·6* | 38747·63 (6) | | | 32596·8 (2) |
| | −*2·6* | | | −*3·0* | | −*2·3* | | | −*3·3* | | −*2·78* | | | |
| | $^4D_2$ = 109031·7 | | | 41072·9 (8) | *189·5* | 41262·4 (4) | *114·9* | 41377·3 (4) | 38562·3 (1) | *188·1* | 38750·41 (3) | *94·10* | 38844·51 (4) | |
| | −*40·1* | | | | | −*39·9* | | −*40·4* | | | −*40·0* | | −*40·48* | |
| | $^4D_1$ = 108991·6 | | | | | 41302·3 (3) | *115·4* | 41417·7 (3) | | | 38790·4 (2) | *94·6* | 38884·99 (4−) | |
| | 3d $^4P_3$ = 108277·67 | 41567·1 (4) | | | | | | | 39315·45 (6) | *188·2* | 39503·6 (2) | | | 33355·14 (6) |
| | −*141·67* | | | | | | | | −*141·54* | | −*142·0* | | | −*141·80* |
| | $^4P_2$ = 108136·00 | | | 41968·9 (2n) | | | | | 39456·99 (4) | *188·60* | 39645·59 (4) | *94·1* | 39739·7 (4) | 33496·94 (5) |
| | −*71·17* | | | | | | | | | | −*71·3* | | −*70·6* | −*71·23* |
| | $^4P_1$ = 108064·83 | | | | | 42231·1 (1) | | | | | 39716·9 (3) | *93·4* | 39810·3 (1) | 33568·17 (4) |

* Detected and classified by Bowen. † Wave-lengths uncertain; see notes in Table I.

Table IV.—Doublet Combinations.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **176149 (7)*** | **158687 (4)*** | $2p'\,^2D = 291500$ | | | | 152047† | | | — |
| **232477 (4)***<br>***−357***<br>**232834 (2)*** | **215017 (2)***<br>***384***<br>**215401 (2)*** | $2p'\,^2P_2 = 235170$<br>*−390*<br>$^2P_1 = 234780$ | | | | 95271† | | | |
| | | $3s\,^2P_2 = 175001{\cdot}15$<br>*384·46*<br>$^2P_1 = 175385{\cdot}61$ | 31495·66 (12) | *390·47* | 31105·19 (6)<br>*384·52*<br>31489·71 (10) | 35558·74 (10)<br>*384·44*<br>35943·18 (5) | *86·80*<br><br>*86·92* | 35471·94 (5)<br>*384·32*<br>35856·26 (6) | 36512·84 (4)<br>*384·67*<br>36897·51 (3) |
| **$2p\,^2D$**<br>**467649** | $2p\,^2P$<br>450187 | | $3p\,^2D_3$<br>143505·49 | *390·44* | $^2D_2$<br>143895·93 | $3p\,^2P_2$<br>139442·42 | *86·86* | $^2P_1$<br>139529·28 | $3p\,^2S_1$<br>138488·28 |
| | | $3d\,^2F_4 = 108250{\cdot}00$<br>*369·92*<br>$^2F_3 = 108619{\cdot}92$ | 35255·49 (9)<br>*369·85*<br>34885·64 (4) | <br><br>*390·30* | <br><br>35275·94 (8) | | | | |
| | | $3d\,^2D_3 = 104491{\cdot}43$<br>*117·98*<br>$^2D_2 = 104609{\cdot}41$ | 39014·03 (4)<br>*118·2*<br>38895·8 (½) | *389·8*<br><br>*390·8* | 39403·8 (½)<br>*117·2*<br>39286·6 (4) | 34951·02 (9)<br>*117·93*<br>34833·09 (3) | <br><br>*86·71* | <br><br>34919·80 (6) | |
| | | $3d\,^2P_2 = 93403{\cdot}2$<br>*−212·4*<br>$^2P_1 = 93190{\cdot}8$ | | | | | | | 45085·0 (5)<br>*−212·4*<br>45297·4 (3) |

* Detected and classified by Bowen. † Lines observed by Millikan and Bowen.

explained, for the terms $3p\,^2\mathrm{D}$, $2p\,^2\mathrm{D}$, from which there resulted a value 468855 for $2p\,^2\mathrm{D}$. As a check, the term $2p\,^2\mathrm{P}$ was similarly estimated from the pair of terms $3p\,^2\mathrm{P}$, $2p\,^2\mathrm{P}$, the value obtained being 450648. The difference, $2p\,^2\mathrm{D} - 2p\,^2\mathrm{P} = 18207$, thus obtained, was in very good agreement with the true figure, 17460, given by Bowen's observations.

A slight modification of these figures was made as the result of a search for combinations between the $2p'$ and $3p$ rows of terms in Table II. The approximate figures obtained show that the wave-numbers of the multiplets, $2p'\,^2\mathrm{D} - 3p\,^2\mathrm{P}$ and $2p'\,^2\mathrm{P} - 3p\,^2\mathrm{P}$, should be respectively of the order, 153000 and 96000, and that the groups should be separated by an interval, 56500, the inexactitude in which arises only from the lack of resolution of the multiple terms involved, and errors of observation. Among the lists of unclassified fluorine lines in the extreme ultra-violet previously given by Millikan and Bowen (*loc. cit.*) there are two lines at $\nu\nu$ 152047, 95271, whose difference is 56776. The identification, though doubtful, seems probable enough to justify the slight amendment of the approximate term values which it would require, and the values of $2p\,^2\mathrm{D}$ and $2p\,^2\mathrm{P}$ have accordingly been chosen as 467649 and 450187, respectively. It should be noted that, if there is any reality in the assumed identification, all the doublet term values are connected by observed lines, and are therefore relatively accurate, whereas in the quartet system the values adopted for the $2p$ and $2p'$ terms are connected with the others only through what is effectively a series formula.

There are several strong lines not included in the analysis. It is possible to associate them in various ways so as to form connected systems of terms, but as no means of checking such systems or of deciding between them has been found, it has been thought best to leave the lines unclassified. In view of their strength and position in the spectrum, it is probable that they arise from terms given in the fourth or fifth column of Table II. There is one multiplet, however, which, on account of the strong probability of its reality, deserves special mention. It is as follows :—

$$\begin{array}{ccccccc}
37671{\cdot}23\,(5) & \mathit{3{\cdot}77} & 37675{\cdot}00\,(4) & \mathit{3{\cdot}40} & 37678{\cdot}40\,(2) & & \\
 & & -\mathit{21{\cdot}78} & & -\mathit{21{\cdot}72} & & \\
 & & 37696{\cdot}78\,(3) & \mathit{3{\cdot}34} & 37700{\cdot}12\,(3+) & \mathit{2{\cdot}46} & 37702{\cdot}58\,(3) \\
 & & & & -\mathit{67{\cdot}43} & & -\mathit{67{\cdot}33} \\
 & & & & 37632{\cdot}69\,(6) & \mathit{2{\cdot}56} & 37635{\cdot}25\,(3)
\end{array}$$

It evidently belongs to the quartet system, and has the form of a PD combination. If, however, the line $\nu$ 37520·9 (4) is included, giving a difference of *114·4* with the line $\nu$ 37635·3, it becomes a DF (or FG, GH, ...) group. In any case the intensities are abnormal. None of the afore-mentioned combinations, occurring among the terms of Table II, would be expected in this region of the spectrum, and the identity of the terms involved therefore remains doubtful.

### *Comparison of the Spectra* O II *and* F III.

The identified terms of the F III spectrum are collected in Table V and compared with the corresponding terms of O II as evaluated by Russell (*loc. cit.*). Since the F III terms are not absolute, and those of the doublet and quartet systems are independently estimated, the only significant features of the comparison relate to the intervals between component terms and the consistency of the ratios between corresponding terms.

It will be observed that most of the intervals in F III are almost exactly double the corresponding intervals in O II. This is particularly noticeable in the quartet system. The most striking exceptions are the $3d\,{}^4D$ and $3d\,{}^4P$ terms. In both spectra the $3d\,{}^4D$ term intervals are partially inverted, but the inverted intervals in F III are complementary to those in O II. In neither case is Landé's interval rule even approximately obeyed. In the $3d\,{}^4P$ terms, on the other hand, the interval rule is obeyed very accurately in F III, and the $3d\,{}^4P_{32}$ interval is again almost exactly double the corresponding interval in O II. The anomaly is due to the abnormally large value of the $3d\,{}^4P_{21}$ interval in O II. In both spectra the terms are inverted.

With the exception of the $2p'$ terms, the ratios of term values increase steadily as the term values decrease, tending towards a value not far from the theoretical ratio of 2·25 for a Coulomb field. This is presumably a further indication that the absolute values chosen for the F III terms are of the right order of magnitude. The $2p'$ terms are very large in F III compared with O II. The abnormality is particularly pronounced in the doublet system, where the ratio exceeds 2·25.

The other exceptional ratios are those of the $3d\,{}^4P_3$, $3p\,{}^2S_1$ and $3d\,{}^2P_2$ terms. With regard to the first of these, it may be remarked that, in addition to the irregular interval value in O II which has already been mentioned, the $3d\,{}^4P$ terms in that spectrum depart from the usual order in being larger than the $3d\,{}^4D$ terms. The F III terms are normal in this respect. A similar remark applies to the $3p\,{}^2S$ term, which is excessively large in O II, and the $3d\,{}^2P_2$ terms. It appears, therefore, in accordance with what has been found in comparing the spectra of other atoms with similar electron structure but different nuclear charges, that the higher the charge the more closely are the empirical rules concerning term magnitudes, interval ratios, etc., obeyed.

## Table V.—Comparison of F III with O II.

| Term values. | | | | Intervals between component terms. | | |
|---|---|---|---|---|---|---|
| Symbol. | F III. | O II. | Ratio $\frac{\text{F III}}{\text{O II}}$ | F III. | O II. | Ratio $\frac{\text{F III}}{\text{O II}}$ |
| (*a*) Quartets. | | | | | | |
| $2p\ {}^4S_2$ | 506000 | 283028 | *1·79* | | | |
| $2p'\ {}^4P_3$ | 354103 | 163190 | *2·17* | −342 | −163 | *2·10* |
| ${}^4P_2$ | 353761 | 027 | | −177 | − 82 | *2·16* |
| ${}^4P_1$ | 584 | 162945 | | | | |
| $3s\ {}^4P_3$ | 181872·5 | 97521·7 | *1·86* | 318·9 | 158·6 | *2·01* |
| ${}^4P_2$ | 182191·4 | 680·3 | | 211·3 | 105·3 | *2·01* |
| ${}^4P_1$ | 402·7 | 785·6 | | | | |
| $3p\ {}^4D_4$ | 149846·0 | 76018·4 | *1·97* | 258·9 | 124·6 | *2·08* |
| ${}^4D_3$ | 150104·9 | 143·0 | | 189·7 | 91·6 | *2·07* |
| ${}^4D_2$ | 294·6 | 234·6 | | 114·9 | 55·5 | *2·07* |
| ${}^4D_1$ | 409·5 | 290·1 | | | | |
| $3p\ {}^4P_3$ | 147592·9 | 74536·7 | *1·98* | 188·7 | 92·0 | *2·05* |
| ${}^4P_2$ | 781·6 | 628·7 | | 94·3 | 46·1 | *2·05* |
| ${}^4P_1$ | 875·9 | 674·8 | | | | |
| $3p\ {}^4S_2$ | 141633·0 | 70859·0 | *2·00* | | | |
| $3d\ {}^4F_5$ | 111384·5 | 51490·7 | *2·16* | 203·7 | 102·3 | *1·99* |
| ${}^4F_4$ | 588·2 | 593·0 | | 155·6 | 77·9 | *2·00* |
| ${}^4F_3$ | 743·8 | 670·9 | | 108·9 | 54·0 | *2·01* |
| ${}^4F_2$ | 852·7 | 724·9 | | | | |
| $3d\ {}^4D_4$ | 108901·6 | 50267·1 | *2·17* | 132·7 | − 42·4 | *−3·13* |
| ${}^4D_3$ | 109034·3 | 224·7 | | − 2·6 | 50·3 | *−0·05* |
| ${}^4D_2$ | 031·7 | 275·0 | | − 40·1 | 34·4 | *−1·17* |
| ${}^4D_1$ | 108991·6 | 309·4 | | | | |

Table V.—Comparison of F III with O II—(continued).

| Term values. | | | | Intervals between component terms. | | |
|---|---|---|---|---|---|---|
| Symbol. | F III. | O II. | Ratio $\frac{\text{F III}}{\text{O II}}$ | F III. | O II. | Ratio $\frac{\text{F III}}{\text{O II}}$ |
| (*a*) Quartets—(continued). | | | | | | |
| $3d\,^4P_3$ | 108277·7 | 50558·1 | *2·14* | −141·7 | − 73·1 | *1·94* |
| $^4P_2$ | 136·0 | 485·0 | | − 71·2 | − 66·5 | *1·08* |
| $^4P_1$ | 064·8 | 418·5 | | | | |
| (*b*) Doublets. | | | | | | |
| $2p\,^2D$ | 467649 | 256200 | *1·83* | | | |
| $2p\,^2P$ | 450187 | 242558 | *1·86* | | | |
| $2p'\,^2D$ | 291500 | 117030 | *2·49* | | | |
| $2p'\,^2P_2$ | 235170 | 70435 | *3·34* | −390 | −173 | *2·25* |
| $^2P_1$ | 234780 | 262 | | | | |
| $3s\,^2P_2$ | 175001·1 | 93952·5 | *1·86* | 384·5 | 180·0 | *2·14* |
| $^2P_1$ | 385·6 | 94132·5 | | | | |
| $3p\,^2D_3$ | 143505·5 | 71308·2 | *2·01* | 390·4 | 190·7 | *2·05* |
| $^2D_2$ | 895·9 | 498·9 | | | | |
| $3p\,^2P_2$ | 139442·4 | 68791·4 | *2·03* | 86·9 | 59·8 | *1·46* |
| $^2P_1$ | 529·3 | 851·2 | | | | |
| $3p\,^2S_1$ | 138488·3 | 79078·7 | *1·75* | | | |
| $3d\,^2F_4$ | 108250·0 | 50061·8 | *2·16* | 369·9 | 211·6 | *1·75* |
| $^2F_3$ | 619·9 | 273·4 | | | | |
| $3d\,^2D_3$ | 104491·4 | 48566·4 | *2·15* | 118·0 | 52·0 | *2·27* |
| $^2D_2$ | 609·4 | 618·4 | | | | |
| $3d\,^2P_2$ | 93403·2 | 49590·8 | *1·88* | −212·4 | −114·0 | *1·86* |
| $^2P_1$ | 190·8 | 476·8 | | | | |

It is disappointing to find no trace of combinations between the $3d\ ^2P$ and the $3p\ ^2D$ and $3p\ ^2P$ terms. The regions of the spectrum concerned have been examined, and the expected lines are definitely missing. Their absence leaves somewhat arbitrary the doublets chosen as the $3s\ ^2P - 3p\ ^2S$ and $3p\ ^2S - 3d\ ^2P$ combinations. In favour of the assignments made are the facts that the resulting terms are of the expected order of magnitude; the intervals are, in the first case, accurate, and in the second consistent, with regard to both magnitude and inversion, with the corresponding O II interval; the lines are strong and obviously important lines in the spectrum, and no other pairs exist with equal claims to adoption. It is interesting to notice also that in O II the combination $3p\ ^2D - 3d\ ^2P$ is absent, although the latter term combines strongly with $3p\ ^2P$ and $3p\ ^2S$.

It is a pleasure to thank Prof. A. Fowler, F.R.S., for his valuable suggestions during the preparation of the paper.

## ADDENDUM.

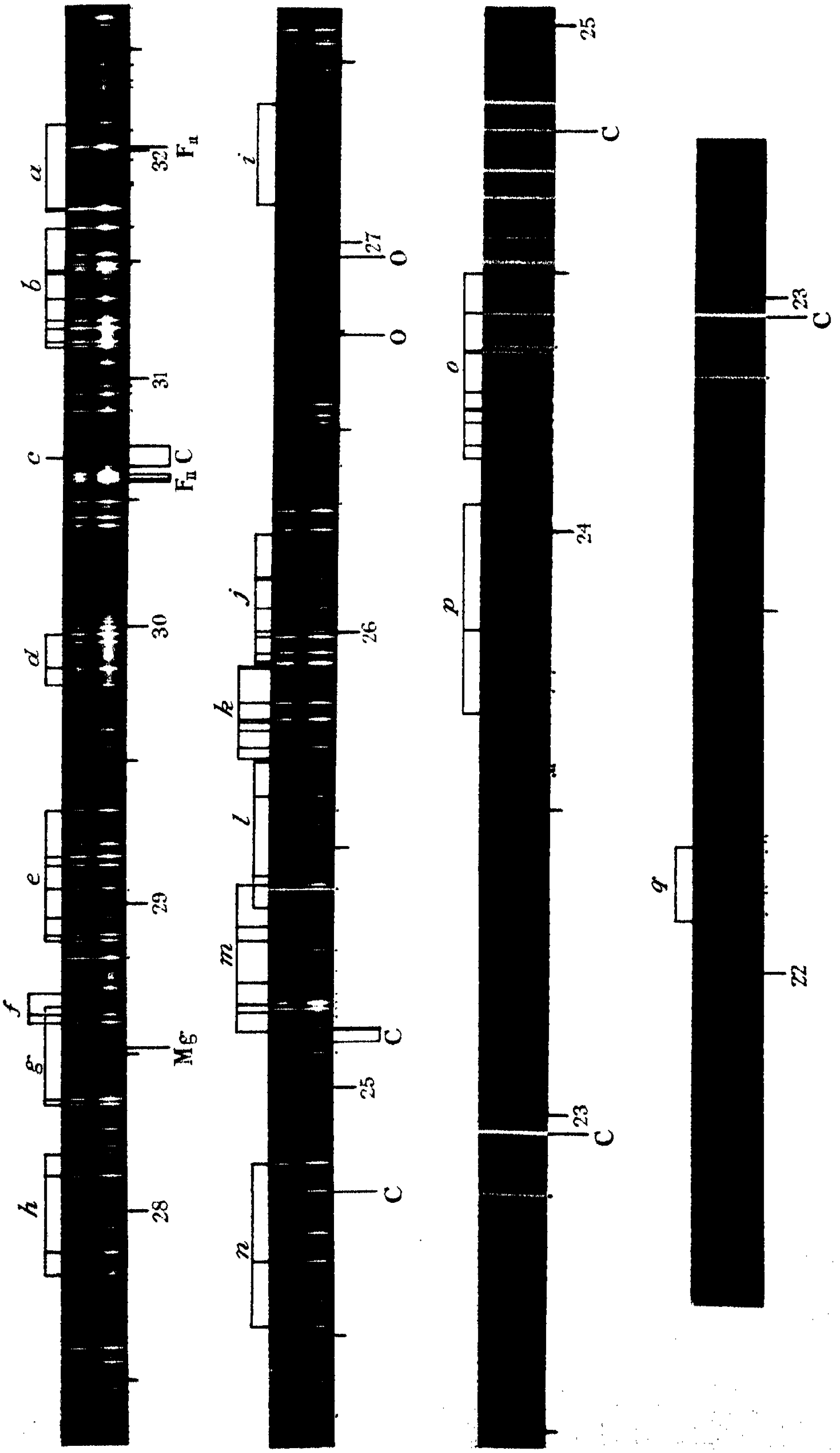
[*Added September* 24, 1928.]—As the FIII spectrum has not previously been described, it has been considered desirable to include reproductions of some of the photographs. These are accordingly given in Plate 7, covering the region λ 3270—λ 2200.

## DESCRIPTION OF PLATE 7.

Spectrum given by powerful discharges through silicon tetrafluoride at low pressure, capillary of "end-on" tube being focussed on slit. Upper two strips taken on quartz Littrow spectrograph, and lower two on quartz spectrograph with separate telescope and collimator, giving smaller dispersion.

Lines not belonging to FIII whose origins are known are indicated below the spectrum—the lines of silicon by small dots and the remainder by chemical symbols. Identified multiplets of FIII are marked above the spectrum, the corresponding term symbols being as follows:—

| | | | |
|---|---|---|---|
| *a* | $3s\ ^2P - 3p\ ^2D$ | *j* | $3p\ ^4D - 3d\ ^4F$ |
| *b* | $3s\ ^4P - 3p\ ^4D$ | *k* | $3p\ ^4P - 3d\ ^4D$ |
| *c* | $3p\ ^4S - 3d\ ^4D$ | *l* | $3p\ ^2D - 3d\ ^2D$ |
| *d* | $3p\ ^4S - 3d\ ^4P$ | *m* | $3p\ ^4P - 3d\ ^4P$ |
| *e* | $3s\ ^4P - 3p\ ^4P$ | *n* | $3s\ ^4P - 3p\ ^4S$ |
| *f* | $3p\ ^2P - 3d\ ^2D$ | *o* | $3p\ ^4D - 3d\ ^4D$ |
| *g* | $3p\ ^2D - 3d\ ^2F$ | *p* | $3p\ ^4D - 3d\ ^4P$ |
| *h* | $3s\ ^2P - 3p\ ^2P$ | *q* | $3p\ ^2S - 3d\ ^2P$ |
| *i* | $3s\ ^2P - 3p\ ^2S$ | | |



Spectrum of Doubly-Ionised Fluorine (F III).

## Summary.

(1) The spectrum of doubly ionised fluorine, obtained by passing strong discharges through silicon tetrafluoride, has been isolated, and 314 lines, extending from λ 3267 to λ 2207, have been measured and tabulated.

(2) The spectrum has been partially analysed into quartet and doublet systems of terms, which have been correlated with the terms to be expected on the Heisenberg-Hund theory, and 82 lines have been classified.

(3) A comparison of the spectrum with that of singly ionised oxygen shows a close correspondence, with a few exceptions which have been discussed.

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# *The Band Spectra of the Alkaline Earth Halides.* I.—CaF, SrF.

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## *Introduction.*

Band spectra of the alkaline earth halides were familiar to the earliest spectroscopic workers. Most of these spectra can be produced in both the flame and arc. The fluorides of calcium,* strontium† and barium‡ all give interesting groups of bands which present obvious regularities, and these have been measured under high dispersion by several observers. The chlorides, bromides, and iodides have not been measured with such precision, although from time to time low dispersion measurements seem to have been made.§ In 1921 Datta|| made a systematic study of the fluorides of calcium, strontium and barium, and, added to these, data of the bands of magnesium fluoride. He gives an excellent plate of photographs of all these spectra and it has, therefore, not been considered necessary to reproduce any spectrograms in the present paper. Constant reference will, however, be made to this plate. Datta's work was principally directed to the discovery of numerical relationships

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* Fabry, 'Astroph. J.,' vol. 21, p. 356 (1907); Rosch, 'Z. Wiss. Photogr.,' vol. 4, p. 384 (1906); Danjon, 'Données Numériques de Spectroscopie,' extrait du vol. 4, p. 144.

† Leopold, 'Z. Wiss. Photogr.,' vol. 11, p. 105 (1913).

‡ George, 'Z. Wiss. Photogr.,' vol. 12, p. 237 (1913).

§ Kayser, 'Handbuch der Spectroscopie,' vols. 5 and 6.

|| 'Roy. Soc. Proc.,' A, vol. 99, p. 436 (1921).

between the molecular weights and corresponding band spectra of these similar compounds. With this in view he labelled the band groups in each spectrum $A_1, A_2, A_3, \ldots, B_1, B_2, B_3, \ldots, C_1, C_2, C_3$, etc., so that analogous groups in the spectra of the various molecules should have the same designation. His selection of analogous spectra was largely based on their general appearance, and Datta gives several numerical relationships of an empirical character on the basis of this assignment. This work was completed before the application of the quantum theory to band spectra became prevalent, and it, therefore, needs revision in the light of our present knowledge. For convenience, however, Datta's designation of the spectra by these letters will be used in referring to them. Mecke* has recently made a quantum analysis of many of these bands and recognised distinct band systems in the fluorides of all the alkaline earths. He has expressed these systems by formulæ of the usual type, and discussed the band structure, the doublet separation, and the vibration frequency shown by this series of similar molecules. The present paper is a continuation and extension of Mecke's work on the analysis of these spectra. The whole of the known band spectra of the fluorides of Mg, Ca, Sr, and Ba have been completely analysed and ordered in regard to their gross structure.

### *General Discussion of the Spectra.*

Under low dispersion very little structure can be seen in these band spectra. A high-power instrument is necessary to separate and measure even the heads. Fine structure analysis is out of the question for CaF, SrF, and BaF; even, with good first order plates taken on a 21-foot grating, the individual band lines are packed close together and not resolved except at great distances from the head. One of the most notable features of these spectra is the existence of unusually prolonged *sequences*, running in some cases to at least 30 members. It is further significant that only one, two, or at most three sequences of any system are ever discerned. The various recorded band systems of each molecule are constituted by the $\Delta n = 0$ and possibly the $\Delta n = \pm 1$ sequences only. $\Delta n = n'' - n'$. (The quadratic formulæ used by Datta and previous workers to express these *sequences* are not of much theoretical significance. After assigning initial ($n'$) and final ($n''$) vibrational quantum numbers to the bands of a system we now prefer to express it by a formula of the type:

$$\nu = \nu_e + (a'n' - b'n'^2 + \ldots) - (a''n'' - b''n''^2 + \ldots), \qquad (1)$$

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* 'Z. Physik,' vol. 42, p. 390 (1927).

which gives explicitly the vibrational constants of the molecule in the initial and final electronic states.) These notable features of the alkaline earth fluoride spectra arise from the circumstance that the vibration frequencies in the initial and final states of the molecule differ by so little. It follows that the moments of inertia I′ and I″, and also the internuclear distances $r_0'$ and $r_0''$ are very nearly equal. Franck* has indicated the mechanism by which changes of vibrational energy take place in a molecule, and it is clear that where, as in this case, the potential energy function of the nuclei is very nearly the same for two electronic states, it will be difficult to effect a change in the number of vibration quanta of the molecule. Hence we find the sequence $\Delta n = 0$ is always dominant, and $\Delta n = \pm 1$ sometimes occur, but are much weaker. Hence also, these molecules have great vibrational stability, and when in addition $b'$ and $b''$ are small, so that the number of vibration quanta required to effect dissociation† is large, we have conditions under which we may expect to find long sequences.

From the approximation of I′ to I″ it follows that $\frac{h}{8\pi^2}\left(\frac{1}{\mathrm{I}'} - \frac{1}{\mathrm{I}''}\right)$, the coefficient of $m^2$ in the expression for the *fine* structure of these bands will be very small. Hence the interval between null line and head will be large. As an example of this we may take the $\mathrm{B}_2\ \mathrm{B}_2'\ \mathrm{B}_2''\ \mathrm{B}_2'''$ groups of bands of CaF. The $\mathrm{B}_2'$ group consists of P heads associated with the $\mathrm{B}_2$ group which are Q heads, while the $\mathrm{B}_2'''$ group of P heads is similarly associated with the $\mathrm{B}_2''$ group of Q heads. Reference to Datta's plate (spectrum 3) emphasises how unfamiliar may be the appearance of a spectrum which results in a special case, such as this, in which the vibrational constants are approximately the same in the initial and final states.

*The Molecular Emitters.*—Within the last three years a number of methods have been adopted and extensively applied to band spectra for the determination of the precise emitters responsible for such radiation. Briefly, these are (1) Study of the absorption spectra of cold gases, and of vapours of known composition produced in the electric furnace ; (2) correlation of the electronic levels of different spectra, so that reliable experimental data by absorption or emission methods as to the origin of one of these fixes the molecule responsible for them all ; (3) comparative methods based on similarities of gross and fine structure. In this connection the multiplicity of the electronic levels determines the emitter as an even or an odd valence-electron molecule, precisely, as in atomic spectra ; (4) fine structure analysis gives the moment of inertia of the emitter, and therefore fixes the nuclear masses within limits which will give a reasonable value to the internuclear distance ; (5) study of isotopy in its effect on both the gross and fine structure is, under favourable conditions, a precise quantitative method.

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* 'Trans. Faraday Soc.,' vol. 21, p. 3 (1925).

† Birge and Sponer, 'Phys. Rev.,' vol. 28, p. 259 (1926).

The series of similar molecules BeF, BO, $CO^+$, CN, $N_2^+$, have, for example, been extensively studied ;† they give rise to similar spectra. All have presumably the same electron structure which is the same externally as that of the sodium atom. There is no room for doubt on theoretical grounds that all the alkaline earth halide spectra are diatomic, and, like the above, are of the one valence-electron type. Direct experimental evidence of this has been obtained recently by Walters and Barratt.‡ For this reason Datta's suggested empirical relationships, based on emitters of the type $XF_2$, and involving the masses of the emitters, are necessarily invalidated. Table I has been constructed showing the diatomic molecules which may reasonably be expected to exist and to have a structure similar to that of the alkaline earth fluorides. Such a table furnishes both the basis for a comparative study of molecular spectra, and suggests directions of research for new band spectra. The molecules marked thus (*) possess band spectra already known.

*The Vibrational Isotope Effect.*—Because of the pronounced crowding together of the heads in sequences, and the frequently low intensity of the sequences $\Delta n = \pm 1$ when present, the alkaline earth fluoride spectra are not very favourable for the study of isotopy. In the case of calcium (atomic weight = 40·07) the two isotopes of masses 40 and 44 will exist in the ratio 56 : 1, so that the isotope effect in the CaF molecule will not be observable.

Table I.

| Probable electron structure. | Molecules. | | | | | |
|---|---|---|---|---|---|---|
| $2 + 2 + 8 + 1$ | BeF* | BO*<br>$CO^+$* | CN*<br>$N_2^+$* | | | |
| $2 + 2 + 8 + 8 + 1$ | MgF* | AlO* | SiN* | PC | BS | BeCl* |
| $2 + 2 + 8 + 16 + 1$ | CaF* | ScO* | TiN | PSi | AlS | MgCl* |
| $2 + 2 + 8 + 18 + 16 + 1$ | SrF* | YO | ZrN | AsSi<br>GeP | AlSe<br>GaS | MgBr*<br>ZnCl |
| $2 + 2 + 8 + 18 + 18 + 16 + 1$ | BaF* | LaO | CeN | SbSi<br>SnP<br>GeAs | AlTe<br>InS<br>GaSe | MgI*<br>CdCl<br>ZnBr |

† Mulliken, 'Phys. Rev.,' vol. 26, p. 561 (1925).

‡ 'Roy. Soc. Proc.,' A, vol. 118, p. 120 (1928).

In the case of strontium (atomic weight = 87·63), the isotopes of masses 88 and 86 would be present in the ratio 4·4 : 1. The resulting isotopic coefficient* for SrF is 1·00206. This is too small in practice to permit of measurement of the effect in spectrograms taken in the first order of a 21-foot grating. The only molecule of the group for which a vibrational isotope effect has been observed and measured is MgF. Details of this case are reserved for another paper.

### *The Existence of Tails to Band Sequences.*

A number of sequences in the CaF and SrF spectra exhibit the phenomenon of a "tail." This occurs when the convergence of the sequence is sufficiently rapid and the intensity of its higher members is appreciable. Its formation is in many respects similar to that of a band head by fine structure lines, but it is not a very common feature of band spectra as the intensity is, as a rule, not sufficiently sustained down the sequence. Datta has recorded the positions of several "tails" in both CaF and SrF systems and has founded certain empirical conclusions upon his data. It would seem well to investigate therefore the theoretical conditions under which tails may be formed.

The heads of a band system are given by equation (1)† :

$$\nu = \nu_e + (a'n' - b'n'^2 + \ldots) - (a''n'' - b''n''^2 + \ldots). \tag{1}$$

A sequence is characterised by $n'' - n' = \text{C}$ (a constant). Substituting for $n'$ in (1) we have

$$\nu = \nu_e - a'\text{C} - b'\text{C}^2 + (a' - a'' + 2b'\text{C})\, n'' - (b' - b'')\, n''^2. \tag{2}$$

The critical value of $n''$ for which a tail is formed is given by $d\nu/dn'' = 0$

$$n_t'' = \frac{a' - a'' + 2b'\text{C}}{2\,(b' - b'')}. \tag{3}$$

For sequences of the $(n, 0)$ type (*i.e.*, defining them by their leading members as the (0, 0), (1, 0), (2, 0) sequences), we obtain, by substituting (3) in (2) and putting $\text{C} = -n'$, for the interval between head and tail

$$\nu_t - \nu_{\text{H}} = \frac{(a' - a'' - 2b'n')^2}{4\,(b' - b'')}. \tag{4}$$

For sequences of the $(0, n'')$ type, *e.g.*, those of which the leading members are (0, 0), (0, 1), (0, 2), etc., we can show similarly by substitution of $(n' + \mathrm{C})$ for $n''$ in equation (1) that

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* Mulliken, 'Phys. Rev.,' vol. 25, p. 119 (1925).

† This is strictly true only if the Q heads are used. The investigation which follows also neglects possible terms of the type $c'n'^3$ and $c''n''^3$, but the extension in this case can easily be made.

$$\nu = \nu_e - a''\mathrm{C} + b''\mathrm{C}^2 + (a' - a'' + 2b''\mathrm{C})\, n' - (b' - b'')\, n'^2, \tag{5}$$

$$n_t' = \frac{(a' - a'' + 2b''\mathrm{C})}{2\,(b' - b'')}, \tag{6}$$

and since $\mathrm{C} = n''$

$$(\nu_t - \nu_{\mathrm{II}}) = \frac{(a' - a'' + 2b''n'')^2}{4\,(b' - b'')}. \tag{7}$$

(*a*) In band systems degraded to the violet $a' > a''$, and usually $b' > b''$, so that by (6) and (7) sequences of the $(0, n'')$ type can always form tails. But for $(n', 0)$ sequences, equation (3) where $\mathrm{C} = -n'$, requires that

$$n' < \frac{a' - a''}{2b'}. \tag{8}$$

(*b*) In band systems degraded to the red side $a' < a''$, and usually $b' < b''$, and therefore by (3) and (4) $(n', 0)$ type sequences will always have tails. The criterion for tail formation by a $(0, n'')$ sequence is that

$$n'' < \frac{a'' - a'}{2b''}. \tag{9}$$

As a general rule $a' \sim a''$ is sufficiently large and the intensity fall down a sequence sufficiently rapid to prevent a tail appearing even though the above theoretical conditions (8) or (9) are satisfied. The alkaline earth fluorides are notably exceptional in this respect, and the above conditions determine the presence or absence of tails satisfactorily.*

### CaF *Systems.*

$\mathrm{A}_4'\,\mathrm{A}_3'$ : $a' = 563 \cdot 39$, $a'' = 583 \cdot 83$, $b' = 1 \cdot 716$, $b'' = 1 \cdot 634$. Owing to the very unusual circumstance that while $a' < a''$, $b' \nless b''$, it is clear from (3) that neither the (1, 0) sequence $\mathrm{A}_3'$ nor the (0, 0) sequence $\mathrm{A}_4'$ can form tails. And from equations (6) and (7) it follows that it would similarly be impossible for any $(0, n'')$ sequence to form a tail even if such sequences existed.

$\mathrm{B}_2$ (*and similarly for* $\mathrm{B}_2''$): $a' = 590 \cdot 285$, $a'' = 584 \cdot 343$, $b' = 3 \cdot 1057$, $b'' = 2 \cdot 8674$. The (0, 0) sequence $\mathrm{B}_2$ (also $\mathrm{B}_2''$), and the (0, 1) sequence $\mathrm{C}_1$ (also $\mathrm{C}_1'$) will have tails. By (8) $n' < \dfrac{5 \cdot 942}{6 \cdot 211}$, therefore the (1, 0) sequence

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* In the examples taken below of CaF and SrF bands the above conditions have been applied and the presence of appreciable cubic terms in the formulæ neglected.

$B_1$ can have no tail. Although the appearance of $B_1$ is at first sight contrary to this conclusion, it will be seen later that our interpretation of the structure of $B_1$ is in complete agreement with the absence of a tail. Experiment shows there are strong tails to $B_2$ and $B_2''$, which should be at about the 13th member, but the tails to $C_1$ and $C_1'$ which should be at about the 26th member will, as Table IV clearly shows, be too weak to see.

### SrF *Systems.*

$A_4' A_3'$ : $a' = 487 \cdot 046$, $a'' = 495 \cdot 003$, $b' = 1 \cdot 8683$, $b'' = 1 \cdot 8243$. The same remarks as were applied to the analogous system of CaF apply here.

$C_1$ (*and similarly* $C_2$) : $a' = 503 \cdot 678$, $a'' = 495 \cdot 811$, $b' = 2 \cdot 256$, $b'' = 2 \cdot 211$. The (0, 0) sequence $C_1$ (also $C_2$), and the (0, 1) sequence $C_3$ (also $C_4$) can form tails, but the (2, 0) and higher sequences, if they existed, could not do so. Experiment shows pronounced tails to the $B_1$ and $B_3$ bands, but those of the $C_1$ (and $C_2$), and the $C_3$ (and $C_4$) sequences are invisible owing to the intensity fall. Equations (3) and (6) show that while the $B_1$ tail is at about (38, 37), the $C_1$ tail is near (87, 87), and the $C_3$ tail near (136, 137).

It will, of course, be clear from equations (4) and (7) that Datta's supposition that $(\nu_t - \nu_H)$ is nearly constant for the various sequences of the same compound is not true. The sequences $B_2$ and $B_2''$ of CaF, and $B_1$ and $B_3$ of SrF on which Datta based his statement, are in both cases, as we shall see later, corresponding sequences associated with the two levels of an electronic doublet. For such, of course, we expect identity.

### *The Calcium Fluoride Band Systems.*

Although measurements of these bands have been made by Fabry, Rosch, Danjon, and Datta, it was found necessary to re-measure all the bands in order to determine some of the relations with certainty. These data were obtained by measurement of two independent sets of plates taken in the first order of a 21-foot grating. They are presented together with the assignment of quantum numbers in Tables II, III and IV. The known calcium fluoride systems fall into three groups : the $A_1A_2$ group in the ultra-violet, the $A_3A_4$ group in the green, and the BC group in the orange.

The $A_1A_2$ group has not been observed on the plates taken, presumably owing to its intrinsic faintness. Probably for the same reason it was not observed in absorption by Walters and Barratt. The wave-length data of Table II are therefore taken from Datta's paper. It is possible that this system may arise from the electron transition $3\,^2S \rightarrow 1\,^2S$, although with this assumption,

Table II.—(Datta's Measurements.)
$3\,^2S \rightarrow 1\,^2S$ (?)

| $n', n''$. | $A_2'$ (Q heads). | | $A_2$ (R heads). | | $n', n''$. | $A_1'$ (Q heads). | | $A_1$ (R heads). | |
|---|---|---|---|---|---|---|---|---|---|
| | λ. | $\nu_{vac.}$ | λ. | $\nu_{vac.}$ | | λ. | $\nu_{vac.}$ | λ. | $\nu_{vac.}$ |
| 0, 0 | — | — | — | — | 1, 0 | — | — | — | — |
| 1, 1 | — | — | · · · | — | 2, 1 | 3373·22 | 29636·74 | 3371·15 | 29655·02 |
| 2, 2 | — | — | | | 3, 2 | 84·64 | 536·77 | 82·62 | 555·41 |
| 3, 3 | — | — | 3449·24 | 28983·66 | 4, 3 | 95·93 | 438·61 | 93·71 | 457·85 |
| 4, 4 | 3462·02 | 28876·70 | 59·95 | 893·88 | 5, 4 | 3407·02 | 342·72 | 3404·76 | 363·28 |
| 5, 5 | 72·78 | 787·25 | 70·59 | 805·33 | 6, 5 | 18·00 | 248·57 | 15·66 | 268·52 |
| 6, 6 | 83·41 | 699·35 | 81·19 | 718·47 | 7, 6 | 28·73 | 156·98 | 26·42 | 176·64 |
| 7, 7 | *93·96 | 612·71 | 91·60 | 631·96 | | | | | |
| 8, 8 | 3504·23 | 528·79 | 3501·80 | 548·59 | | | | | |
| 9, 9 | 14·46 | 445·78 | 11·84 | 467·00 | | | | | |
| 10, 10 | 24·54 | 364·45 | — | — | | | | | |

* = Value smoothed before applying Method of Least Squares.

the three levels 1S, 2S, 3S, do not form a Rydberg series. Comparison of the molecular levels (see fig. 1) with those of the similar atom $Ca^+$ does not, however, suggest any level other than $3\,^2S$ for the upper one. We may, therefore, deny that the above analogy of molecular and atomic levels has any completeness,—in which case the character of the upper level is unknown, or, we may not expect to find the levels of such complex molecules as these fitting a Rydberg formula. In the following text we shall, for convenience, describe the level as $3\,^2S$, but quite tentatively. The magnitude of the electronic jump involved—about 29250 ν, which is considerably greater than any others in this molecule—is strongly in support of its being a transition to the ground level. The $A_2'$ and $A_1'$ sequences are all Q branches, the $A_2$ and $A_1$ sequences, respectively, are the associated R heads. We shall consider shortly the ($A_4A_3$) system which is of similar structure, and is very probably due to the electron $2\,^2S \rightarrow 1\,^2S$. Here also $A_4$ and $A_4'$ are respectively R and Q branches of the (0, 0) sequence, while $A_3$ and $A_3'$ are R and Q branches of the (1, 0) sequence.

The presence of strong Q branches in a $^2S \rightarrow {}^2S$ transition is exceptional and calls for comment. Mulliken† has recently shown that for this type of transition—if we assume Hund's case *b* type of electron spin—weak Q branches are to be expected. In addition he has remarked (*vide* p. 149) that for the B bands of CaH, the $^2S$ state is of an unusual type (possibly one in which $\sigma_k \neq k$), and he suggests that this molecular $^2S$ state may be derived from one of the low-lying P or D states of the calcium atom. Some such postulate would seem to be necessary for all the alkaline earth fluorides, for which the $^2S \rightarrow {}^2S$ transitions present unusual features.

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† 'Phys. Rev.,' vol. 30, p. 138 (1927).

In expressing the band systems by formulæ of type (1), or, more generally with cubic terms, the Q heads have been used, and, owing to the unusual circumstance of two long sequences constituting the system, it was thought to be most accurate to proceed as follows. The (0, 0) and (1, 0) sequences are given by

$$\left.\begin{array}{ll} \nu = \nu_e + (a' - a'')\,n'' - (b' - b'')\,n''^2 + (c' - c'')\,n''^3 & (0,\,0) \\ \nu = \nu_e + a' - b' + c' + (a' - a'' - 2b' - 3c')\,n'' & \\ \qquad\qquad - (b' - b'' - 3c')\,n''^2 + (c' - c'')\,n''^3 & (1,\,0) \end{array}\right\} . \quad (10)$$

The *sequences* were therefore fitted independently to cubic formulæ using the Method of Least Squares developed by Birge and Shea.[*] The values of the constants $a'$, $b'$, $c'$, $a''$, $b''$ and $c''$ can then be deduced at once from (10). By this method the data of Table I gave for these sequences.

$$(A_2') \quad \nu = 29252{\cdot}375 - 97{\cdot}5766\,n'' + 0{\cdot}93940\,n''^2 - 0{\cdot}006111\,n''^3$$

$$(A_1') \quad \nu = 29738{\cdot}479 - 102{\cdot}5882\,n'' + 0{\cdot}82464\,n''^2 + 0{\cdot}020000\,n''^3$$

with probable errors in $\nu$ of 0·024 and 0·045 respectively. Hence we obtain

$$\nu_e = 29252{\cdot}375 \quad \left.\begin{array}{llll} a' = 488{\cdot}705 & b' = 2{\cdot}5632 & c' = & -0{\cdot}03825 \\ a'' = 586{\cdot}282 & b'' = 3{\cdot}5026 & {}^\dagger c'' = & \left\{\begin{array}{l} -0{\cdot}03214\,(A_2') \\ -0{\cdot}05825\,(A_1') \end{array}\right. \end{array}\right\} . \quad (11)$$

The data for the band system in the green region of the spectrum are given in Table III. (It may be mentioned that micrometer settings in the measurement of all the spectrograms were made on the extreme *edge* of the bands.) This system, as already mentioned, is attributed to the $2\,^2S \rightarrow 1\,^2S$ transition, and is of similar structure to the one already considered. Its data have been dealt with by the above method and we find for the sequences (Q heads only):

$$(A_4') \quad \nu = 18888{\cdot}136 - 20{\cdot}4411\,n'' - 0{\cdot}08214\,n''^2 - 0{\cdot}001047\,n''^3$$

$$(A_3') \quad \nu = 19449{\cdot}786 - 23{\cdot}8058\,n'' - 0{\cdot}14949\,n''^2 - 0{\cdot}000035\,n''^3$$

with probable errors in $\nu$ of 0·028 and 0·034 respectively.

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[*] 'Univ. California Publ. Maths.,' vol. 2, p. 67 (1927).

[†] From equation (10) we note that the coefficients of $n''^3$ should be the same for $A_2'$ and $A_1'$, also for $A_4'$ and $A_3'$. In practice they are unequal, chiefly due to neglect of higher power terms and experimental errors. Alternative values of $c''$ therefore arise.

Table III.

$2\,^2S \rightarrow 1\,^2S$.

| $n'$, $n''$. | Int. | $A_4'$ (Q heads). |  | Int. | $A_4$ (R heads). |  | $n'$, $n''$. | Int. | $A_3'$ (Q heads). |  | Int. | $A_3$ (R heads). |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | λ. | $\nu_{vac.}$ |  | λ. | $\nu_{vac.}$ |  |  | λ. | $\nu_{vac.}$ |  | λ. | $\nu_{vac.}$ |
| 0, 0 | 9 | 5292·855 | 18888·15 | 10 | 5291·002 | 18894·70 | 1, 0 | — | — | — | — | — | — |
| 1, 1 | 8 | 98·62 | 67·60 | 8 | 96·847 | 73·92 | 2, 1 | 0 | 5146·362 | 19425·80 | 0 | 5145·394 | 19429·46 |
| 2, 2 | 8 | 5304·44 | 46·90 | 8 | 5302·726 | 52·99 | 3, 2 | 1 | 52·77 | 01·62 | 1c | 51·862 | 05·07 |
| 3, 3 | 7 | 10·32 | 26·03 | 7 | 08·68 | 31·85 | 4, 3 | 2 | 59·31 | 19377·05 | 2 | 58·38 | 19380·55 |
| 4, 4 | 7 | 16·24 | 05·07 | 6 | 14·69 | 10·55 | 5, 4 | 2 | 65·94 | 52·19 | 2 | 65·02 | 55·63 |
| 5, 5 | 5c | *22·24 | 18783·87 | 5c | 20·72 | 18789·24 | 6, 5 | ? | 72·7 | 26·90 | 1 | 71·79 | 30·30 |
| 6, 6 | 5c | *28·26 | 62·65 | 5 | 26·858 | 67·59 | 7, 6 | 2 | 79·486 | 01·58 | 2 | 78·628 | 04·77 |
| 7, 7 | 5 | 34·515 | 40·65 | 5 | 33·09 | 45·65 | 8, 7 | 2 | 86·394 | 19275·87 | 2 | 85·56 | 19278·96 |
| 8, 8 | 4 | 40·715 | 18·89 | 4c | 39·254 | 24·01 | 9, 8 | 1 | 93·44 | 49·71 | 1 | 92·61 | 52·79 |
| 9, 9 | 4 | 47·03 | 18696·78 | 4c | 45·62 | 01·72 | 10, 9 | 1 | 5200·538 | 23·44 | 1 | 99·747 | 26·37 |
| 10, 10 | 3 | 53·41 | 74·50 | 3 | 52·074 | 18679·16 | 11, 10 | 1 | 07·78 | 19196·72 | 1 | 5206·99 | 19199·63 |
| 11, 11 | 3 | *59·78 | 52·31 | 3c | 58·64 | 56·28 | 12, 11 | — | — | — | 1c | 14·31 | 72·67 |
| 12, 12 | 3c | 66·43 | 29·19 | 3 | 65·22 | 33·40 | 13, 12 | 1 | †22·56 | 42·38 | 1c | 21·765 | 45·30 |
| 13, 13 | 3c | 73·06 | 06·21 | 3 | 71·87 | 10·33 | 14, 13 | 0 | †30·00 | 15·15 | 0 | 29·28 | 17·79 |
| 14, 14 | 3c | 79·8 | 18582·9 | 3c | 78·65 | 18586·87 | 15, 14 | 0c | †37·7 | 19087·05 | 0 | 36·87 | 19090·08 |
| 15, 15 | 3 | 86·583 | 59·50 | 3 | 85·53 | 63·13 | 16, 15 | 0 | †45·29 | 59·43 | 0 | 44·66 | 61·72 |
| 16, 16 | 3 | 93·44 | 35·90 | 2 | 92·28 | 39·89 | 17, 16 | 0 | †53·10 | 31·10 | 0 | 52·40 | 33·63 |
| 17, 17 | 3 | 5400·48 | 11·74 | 2c | 99·50 | 15·10 |  |  |  |  |  |  |  |
| 18, 18 | 2c | 07·58 | 18487·44 | 1 | 5406·56 | 18490·92 |  |  |  |  |  |  |  |
| 19, 19 | — | — | — | 1c | 13·9 | 65·7 |  |  |  |  |  |  |  |
| 20, 20 | 2 | 21·995 | 38·28 | 2 | 21·06 | 41·46 |  |  |  |  |  |  |  |

* Value smoothed before computation.

† Value omitted in computation.

Hence we obtain by applying equation (10)

$$\nu_e = 18888 \cdot 136 \quad \left. \begin{array}{l} a' = 563 \cdot 388 \quad b' = 1 \cdot 7160 \quad c' = \quad -0 \cdot 02245 \\ a'' = 583 \cdot 829 \quad b'' = 1 \cdot 6339 \quad {}^{*}c'' = \left\{ \begin{array}{l} -0 \cdot 02140 \ (\mathrm{A}_4') \\ -0 \cdot 02241 \ (\mathrm{A}_3') \end{array} \right. \end{array} \right\} . \quad (12)$$

As already mentioned, an unusual feature is apparent, viz., that while $a' < a''$, $b' > b''$. As a result of this, the successive heads of both sequences diverge with increasing quantum number, since $(\omega_n' \sim \omega_n'')$ becomes greater. As a result $\mathrm{I}_n'$ and $\mathrm{I}_n''$ differ increasingly, and therefore $\frac{h}{8\pi^2}\left(\frac{1}{\mathrm{I}'} - \frac{1}{\mathrm{I}''}\right)$ increases, and so the Q–R interval diminishes with increasing $n$. This is confirmed by Table III. It will be noted that the (1, 0) band of the system was too faint to be recorded on the plates taken, and this band has in fact never been recorded hitherto. Nevertheless, there is no reason to doubt the correctness of the assignment made, on the basis of which the system shares its final state in common with two others. Attention must be drawn to the discrepancies between the final vibrational constants of (11) and (12). The incomplete and possibly less accurate data of Datta in Table II may account to some extent for the difference in $a''$, but the wide difference in the values of $b''$ is difficult to explain. When it is recalled that the faint system designated $3\,{}^2\mathrm{S}$ (?) → $1\,{}^2\mathrm{S}$ has not been recorded on our plates, or on those of any other worker except Datta, it seems not impossible that it *may* have an origin in some molecule other than CaF.

With reference to the (0, 0) sequence of the $(\mathrm{A}_4\mathrm{A}_3)$ system, Walters and Barratt have drawn attention to the notably different appearance in emission and absorption. This difference is essentially twofold: (1) a redistribution of intensity in the sequence, and (2) the absence of sharply defined heads in absorption, resulting in an apparently different structure. These workers have suggested that pressure may be a factor of importance, since in the presence of foreign gases the structure observed at low pressure in absorption is replaced by continuous spectrum. They also, of course, recognise the different temperature conditions in which the absorption and emission spectra are produced. The present investigation has thrown no additional light upon this problem but I incline to the opinion that the temperature factor is adequate to explain both the above features. A very similar case is found in the violet CN bands—which also are a $2\,{}^2\mathrm{S} \rightarrow 1\,{}^2\mathrm{S}$ transition. Reference to Plates 13 and 14 in a

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[*] *See* note † on p. 169.

paper by Jevons* shows (*a*) the effect of low temperature conditions in displacing energy into the higher members of a band sequence (spectrum 3), and (*b*) the apparent non-coincidence of structure which may result from a temperature re-distribution of energy among the rotational states. Precisely these factors are apparent in the CaF sequence in question, although the temperature conditions here are not in so great a contrast as those under which the CN bands exhibited the modifications to which we have referred. The effect of temperature on the *vibrational* structure must, however, be indirect, and it is in the mechanism of this that the real mystery lies. If, for example, the distribution of vibrational energy was governed directly by temperature considerations then it could be calculated from the principle of equipartition of energy. Thus, for the molecule in question, it is easy to show that a temperature of over 7000° C. is necessary to make the vibrational state $n = 5$ the most probable, while at 1100° C. the state $n = 0$ is still somewhat more probable than $n = 1$. This latter temperature is about that at which Walters and Barratt used their absorption furnace. Their absorption spectrogram of this CaF sequence shows a maximum at about $n = 4$ (the 5th head). Apart from the mechanism of this temperature effect on vibration, it remains to be explained why it makes itself so apparent in this particular band system, and not in the other system of CaF ($2\,^2P \rightarrow 1\,^2S$) shortly to be described. It seems to the writer that a clue may possibly be found in the $^2S \rightarrow {}^2S$ character of the electron transition, which is the same as that of the CN bands previously mentioned.

The third important group of CaF bands is found in the yellow and orange region. These are all degraded to the violet side and comprise the band sequences designated by the letters B and C by Datta. The present writer's measurements together with a quantum analysis of these bands are given in Table IV. A few of the P heads associated with the $C_1'$ sequence, and previously unrecorded, have been measured on the plates taken. The assignment of vibrational quantum numbers to these P heads is uncertain. The ($n'$, $n''$) values of the table may possibly require diminishing by one unit or more. The same ambiguity occurs later, in connection with the analogous SrF bands. The comparative weakness of P heads as compared with Q heads is notable throughout the whole system. (The $B_2'$ sequence has a spurious enhanced intensity by reason of the background of structure arising from the $B_2''$ sequence.)

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[*] 'Roy. Soc. Proc.,' A, vol. 112, p. 407 (1926).

## Table IV.

$(2\,^2P_1 \rightarrow 1\,^2S)$ $2\,^2P \rightarrow 1\,^2S$ $(2\,^2P_2 \rightarrow 1\,^2S)$

| $n', n''$. | Int. | $B_1$ (Q heads). | | Int. | $B_1'$ (P heads). | | $n', n''$. | Int. | $B_2''$ (Q heads). | | Int. | $B_2'''$ (P heads). | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $\lambda$. | $\nu_{vac.}$ | | $\lambda$. | $\nu_{vac.}$ | | | $\lambda$. | $\nu_{vac.}$ | | $\lambda$. | $\nu_{vac.}$ |
| 0, 0 | 6 | 6036·919 | 16560·17 | 6 | 6050·780 | 16522·23 | 0, 0 | 10 | 6064·396 | 16485·14 | 5 | 6086·908 | 16424·17 |
| 1, 1 | 6c | 34·84 | 65·87 | 5c | 48·80 | 27·64 | 1, 1 | 9 | 62·339 | 90·73 | 5 | 84·963 | 29·41 |
| 2, 2 | 5 | 32·90 | 71·20 | 4 | 46·893 | 32·85 | 2, 2 | 8 | 60·418 | 95·96 | 4 | 83·176 | 34·24 |
| 3, 3 | 5 | 31·095 | 76·16 | 4c | 45·258 | 37·32 | 3, 3 | 7 | 58·624 | 16500·84 | 4 | 81·566 | 38·59 |
| 4, 4 | 4 | 29·29 | 80·84 | 3 | 43·642 | 41·74 | 4, 4 | 6 | 56·957 | 05·38 | 2 | 80·16 | 42·39 |
| 5, 5 | 4c | 27·755 | 85·34 | 3c | 42·204 | 45·68 | 5, 5 | 5 | 55·45 | 09·49 | 2 | 78·825 | 46·00 |
| 6, 6 | 4c | 26·02 | 90·12 | 3 | 40·89 | 49·28 | 6, 6 | 5 | 54·027 | 13·37 | ? | 77·60 | 49·32 |
| 7, 7 | 4c | 24·29 | 94·88 | | | | 7, 7 | 4 | 52·794 | 16·73 | ? | 76·30 | 52·84 |
| | | | | | | | 8, 8 | 4 | 51·606 | 19·98 | | | |
| | | $C_1$ (Q heads). | | | (P heads). | | | | $C_1'$ (Q heads). | | | (P heads). | |
| 0, 1 | 4 | 6256·602 | 15978·71 | | | | 0, 1 | 3 | 6285·35 | 15905·62 | | | |
| 1, 2 | 3 | 52·155 | 990·07 | | | | 1, 2 | 4 | 80·87 | 16·99 | | | |
| 2, 3 | 3 | 47·826 | 16001·15 | | | | 2, 3 | 4 | 76·541 | 27·95 | | | |
| 3, 4 | 2 | 43·71 | 11·70 | | | | 3, 4 | 5 | 72·37 | 38·54 | 0 | 6296·59 | 15877·23 |
| 4, 5 | 3c | 39·763 | 21·82 | | | | 4, 5 | 5 | 68·368 | 48·71 | 0 | 92·26 | 888·15 |
| 5, 6 | 3c | 35·96 | 31·60 | | | | 5, 6 | 4 | 64·548 | 58·44 | 1 | 88·09 | 898·69 |
| 6, 7 | 2 | 32·275 | 41·07 | | | | 6, 7 | 3c | 60·875 | 67·80 | 0 | 84·09 | 908·81 |
| 7, 8 | ? | — | — | | | | 7, 8 | 4 | 57·374 | 76·74 | 0 | 80·26 | 918·51 |
| 8, 9 | 2 | 25·69 | 58·04 | | | | 8, 9 | 3c | 54·07 | 85·18 | | | |
| 9, 10 | 3 | 22·31 | 66·77 | | | | 9, 10 | 3 | 50·255 | 94·93 | | | |

Table IV—(continued).

$2\,{}^2P_1 \rightarrow 1\,{}^2S$.

| $n'$, $n''$. | Int. | $B_1$ (Q heads). | |
|---|---|---|---|
| | | λ. | $\nu_{vac.}$ |
| 4, 3 | 5 | 5830·786 | 17145·60 |
| 5, 4 | 6 | 31·11 | 44·65 |
| 6, 5 | 6 | 31·494 | 43·52 |
| 7, 6 | 6 | 32·01 | 42·00 |
| 8, 7 | 6 | 32·637 | 40·16 |
| 9, 8 | 5 | 33·384 | 37·97 |
| 10, 9 | 5 | 34·226 | 35·50 |
| 11, 10 | 5 | 35·21 | 32·60 |
| 12, 11 | 5 | 36·305 | 29·39 |
| 13, 12 | 5 | 37·52 | 25·83 |
| 14, 13 | 5 | 38·90 | 21·78 |
| 15, 14 | 5 | 40·386 | 17·42 |
| 16, 15 | 5 | 42·02 | 12·64 |
| 17, 16 | 5 | 43·80 | 07·42 |
| 18, 17 | 5 | 45·783 | 01·62 |
| 19, 18 | 3 ? | 47·87 | 17095·52 |

The $B_1$ sequence (of Q heads) calls for special comment. At first sight it appears to be similar to the (0, 0) sequences, and run to a pronounced tail at about λ 5830. It has been regarded as such by Datta and others. On this basis, however, it has not been found possible to include it in the general scheme. I believe it rather to be a sequence beginning at λ 5830 (ν. 17146), and proceeding outwards to the less refrangible side. On this view $B_1$ becomes the (1, 0) sequence associated with $B_2$ and $C_1$, *i.e.*, arising from the upper ${}^2P_1$ level. There are two considerations which at first sight appear to be unfavourable to this view. (1) The analogue of $B_1$ arising from the ${}^2P_2$ level is very much less intense (for some unknown reason), there being only a slight fogging of the plate where it should be located. (2) The intensity of the sequence appears to fall suddenly after the band (18, 17); the band (19, 18) is weak, and the band (20, 19) is quite invisible. It will be shown, however, in the section on the Heat of Dissociation of the Molecule, that this peculiar feature gives strong support to the interpretation.

The sequences $C_1$, $B_2$, and $B_1$ are given by :—

$$(C_1)\quad \nu = 15966{\cdot}771 + 12{\cdot}1691n'' - 0{\cdot}25345n''^2 + 0{\cdot}004444n''^3,$$

$$(B_2)\quad \nu = 16560{\cdot}167 + 5{\cdot}9426n'' - 0{\cdot}23829n''^2 + 0{\cdot}011296n''^3,$$

$$(B_1)\quad \nu = 17146{\cdot}716 + 0{\cdot}0094n'' - 0{\cdot}12087n''^2 - 0{\cdot}002092n''^3.$$

Now the (0, 0) and (0, 1) sequences of a band system are :—

$$\left.\begin{array}{ll}(0,1) & \nu = \nu_e - a' - b' - c' + (a' - a'' + 2b' + 3c')\,n'' \\ & \qquad - (b' - b'' + 3c')\,n''^2 + (c' - c'')\,n''^3 \\ (0,0) & \nu = \nu_e + (a' - a'')\,n'' - (b' - b'')\,n''^2 + (c' - c'')\,n''^3\end{array}\right\}, \quad (13)$$

so that from $C_1$ and $B_2$ we obtain

$$\left.\begin{array}{ll} & a' = 590{\cdot}2853 \; b' = 3{\cdot}10567 \;\; c' = +0{\cdot}005053 \\ \nu_e = 16560{\cdot}167 & \\ & a'' = 584{\cdot}3427 \; b'' = 2{\cdot}86738 \;\; c'' = \begin{cases} +0{\cdot}000609\,(C_1) \\ -0{\cdot}006243\,(B_2)\end{cases}\end{array}\right\}. \quad (14)$$

If we use $B_2$ and $B_1$ we obtain from equation (10) :—

$$\left.\begin{array}{ll} & a' = 589{\cdot}4177 \;\; b' = 2{\cdot}90787 \;\; c' = +0{\cdot}03914 \\ \nu_e = 16560{\cdot}167 & \\ & a'' = 583{\cdot}4751 \;\; b'' = 2{\cdot}66958 \;\; c'' = \begin{cases} +0{\cdot}02784(B_2) \\ +0{\cdot}04123(B_1)\end{cases}\end{array}\right\}. (14')$$

The discrepancy between the constants of (14) and (14′) possibly arises from the fact that the equation for $B_1$ includes members up to (19, 18), the disposition of which may require higher power terms, while the expressions for $B_2$ and $C_1$ were obtained from data on 6 or 7 heads only.

Treating similarly the (0, 0) and (0, 1) sequences associated with the other level of the doublet $2\,{}^2P_2$ we find that they are expressed by

$$(B'') \quad \nu = 16485{\cdot}130 + \;\; 5{\cdot}8003n'' - 0{\cdot}19158n''^2 + 0{\cdot}001330n''^3,$$

$$(C_1') \quad \nu = 15893{\cdot}200 + 12{\cdot}6542n'' - 0{\cdot}37718n''^2 + 0{\cdot}012605n''^3.$$

By equation (13) we then obtain

$$\left.\begin{array}{ll} & a' = 588{\cdot}534 \;\; b' = 3{\cdot}3341 \;\; c' = +0{\cdot}061866 \\ \nu_e = 16485{\cdot}130 & \\ & a'' = 582{\cdot}734 \;\; b'' = 3{\cdot}1426 \;\; c'' = \begin{cases} +0{\cdot}060536\,(B_2'') \\ +0{\cdot}049261\,(C_1')\end{cases}\end{array}\right\}. (15)$$

Comparing with the constants of (14) it is clear that there is a small but quite definite difference in the vibrational constants of the molecule for the two levels $2\,{}^2P_1$ and $2\,{}^2P_2$. The vibrational structure of the $2\,{}^2P_2$ level is characterised by a considerably larger term in $n^3$. Incidentally, the $^2P$ level is an inverted *doublet* level, and the appropriate designation has been made in Tables IV and V.

Comparing (14), (14′), and (15) with (12) it will be seen that there is fair agreement in the case of $a''$, but a very marked discrepancy in $b''$. (The values of $c''$ are unreliable for purposes of comparison, for the reason explained in a footnote.) I am not at present able to offer any suggestion as to the cause of the discrepancy in $b''$, but I am convinced of its reality, and that it must arise from some fundamental feature in the structure of the alkaline earth fluoride molecules. Under other circumstances a discrepancy of this order would cast some considerable doubt on the identification of the final levels of these two systems with each other. There is, however, little room to doubt that the systems are related as indicated. There is close agreement between the values of $a''$. In addition, they are both resonance systems of CaF, as is shown by the work of Walters and Barratt in absorption.

Table V collects our knowledge of the various levels of the CaF molecule. For the constants of the ground level $1\,^2S$, the mean of the values from equations (12), (14) and (15) has been placed in Table V, but for specific purposes the precise values of these equations must be used.

Table V.

| Level. | Energy. |  | $a$ ($\omega_0$). | $b$ ($\omega_0 x$). | $c$. |
|---|---|---|---|---|---|
|  | $\nu$. | Volts. |  |  |  |
| $1\,^2S$ | 0 | 0 | 583·63 | 2·548 | ? |
| $2\,^2P_2$ | 16485·13 | 2·035 | 588·534 | 3·3341 | +0·061866 |
| $2\,^2P_1$ | 16560·17 | 2·044 | 590·285 | 3·1057 | +0·005053 |
| $2\,^2S$ | 18888·14 | 2·332 | 563·388 | 1·7160 | −0·02245 |
| $3\,^2S$ (?) | 29252·37 | 3·611 | 488·705 | 2·5632 | −0·03825 |

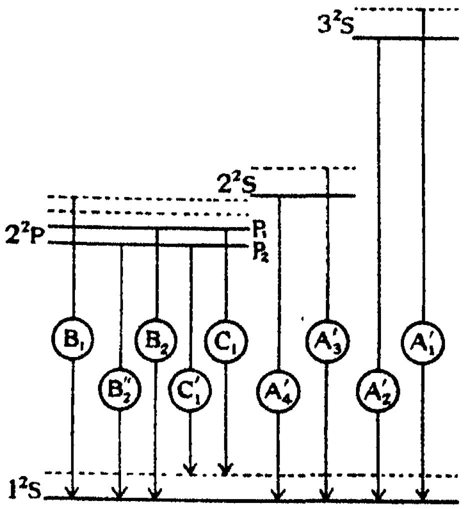

FIG. 1.—Energy Levels of the CaF Molecule.

Fig. 1 represents the complete scheme of transitions in the CaF molecule. The dotted levels are vibrational levels. To avoid confusion, only the transition corresponding to the *leading* member of each sequence has been inserted.

### *Heat of Dissociation of the* CaF *Molecule.*

Applying the methods of Birge and Sponer,* the energy of dissociation of the CaF molecule has been evaluated from the vibrational structure of the various electronic levels. As a rule, the critical value of $n$ which makes $\omega_n = 0$ is imaginary if the coefficient $c$ is positive, but in other cases satisfactory results have been obtained. For the $1\,^2S$ level we find from the data of (12) that $D'' = 25588\,.\,\nu$ and from (14) that $D'' = 25241\,.\,\nu$. Approximately we may take $D''$ as $25400\,.\,\nu$. From the $2\,^2S$ level we obtain $D' = 42218\,.\,\nu$ and from the $3\,^2S$ (?) level $D' = 42589\,.\,\nu$. If we take the drastic step of neglecting the cubic term in the case of $2\,^2P_2$ and $2\,^2P_1$ we get values which are remarkably close to these, viz., $D'' = 27014$ and $D' = 42457$ and $44608\,.\,\nu$. The best value of $D'$ is probably about $42400\,.\,\nu$. The difference $D' - D'' \doteq 17000$ (or less), must correspond to residual electronic energy in either the calcium or fluorine atom resulting from dissociation. It is probably associated with the calcium atom, for it is from this atom the valence electron of the molecule arises. The resonance transition in the Ca atom is $1\,^1S - 2\,^3P$ ($15210\ \nu$). If we assume the calcium atom produced by dissociation to be in a $2\,^3P$ state, we can derive $D''$ from the more reliable value of $D'$ ($= 42400\,.\,\nu$). This gives

$$D'' = 27200\,.\,\nu = 3\cdot36 \text{ volts} = 77460 \text{ cals.} \tag{16}$$

One other possibility may be mentioned. Following Mulliken's suggestion mentioned on p. 168, *if* the normal $1\,^2S$ state of the valence electron in the CaF *molecule* can be identified energetically with the $2\,^3P$ state in the calcium *atom*, then it is probable that the calcium atom liberated by dissociation of the excited molecule will be in a $1\,^3S$ state (where $2\,^3P - 1\,^3S = 16300\,.\,\nu$). If this is the case then taking $D'$ as $42400\,.\,\nu$ we should have $D'' = 26100\,.\,\nu = 3\cdot22$ volts $= 74330$ cals.

The value found for the energy of dissociation of the CaF molecule has an important bearing on the sudden fall of intensity and termination of the $B_1$ sequence with the member (19, 18). It will be seen from Table IV that (18, 17) band is strong, the (19, 18) band considerably weaker, and all higher members are absent. If by means of equation (14′) we evaluate the initial energy of the molecule when these bands would be radiated, we find for $n' = 18$, $\nu = 26456$; for $n' = 19$, $\nu = 26978$; and for $n' = 20$, $\nu = 27498$. Since the value of the energy of dissociation is about 27200 . ν, it is reasonable to suppose that beyond $n' = 19$ vibrational instability will set in, resulting in a sudden termination of the sequence. Fig. 2 will make this feature clearer. An analogous case is found in the first positive band spectrum of nitrogen. The peculiar selection of the bands of this spectrum, which constitutes the nitrogen afterglow, is explained on the assumption that in the electronic state $2\,^3P$, 11 vibration quanta load the $N_2$ molecule with energy equal to the dissociation value.

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* *Loc. cit.*

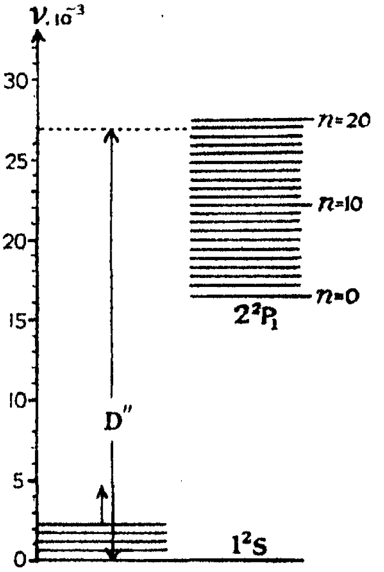

FIG. 2.

### *The Band Spectra of* SrF.

Like the band systems of CaF, these also fall into three groups, (1) an $A_1A_2$ group in the near ultra-violet, first recorded by Datta, (2) an $A_3A_4$ group in the yellow-green region. (3) a BC group of a more complex character extending from the orange to the extreme red. Like their counterparts in CaF we find that the first two groups are degraded to the red side and the third group to the violet side. They also appear to arise from the same electronic transitions $3\,^2S \rightarrow 1\,^2S$, $2\,^2S \rightarrow 1\,^2S$, and $2\,^2P \rightarrow 1\,^2S$ respectively. All the systems exhibit minor doublet intervals due to the presence of Q branches; the Q heads, it will be noted, are always stronger than the associated P or R heads. The presence of strong Q branches in $^2S \rightarrow {}^2S$ transitions is notable, and the remarks made in connection with the analogous CaF bands apply here. It was found desirable to re-measure the SrF bands, and this was done from good plates taken in the first order of a 21-foot Rowland grating. (Micrometer settings were uniformly made on the extreme edges of bands.) The spectrograms taken of the $C_3$, $C_3'$, $C_4$, $C_4'$ sequences were rather fragmentary, and for purposes of Table VIII and the subsequent analysis Leopold's more complete data have been recorded (after subtraction of some 4·70 . ν to bring them into agreement with such of the bands as were measured on my plates). The measurements of the ultra-violet sequences $A_1$, $A_1'$, $A_2$, $A_2'$ recorded by Datta have also been adopted in Table VI as here also, owing to their faintness, only a fragmentary record was obtained on the plates taken.

Table VI.—(Datta's Measurements.)

$3\,^2S$ (?) → $1\,^2S$.

| $n', n''$. | $A_2'$ (Q heads). |  | $A_2$ (R heads). |  | $n', n''$. | $A_1'$ (Q heads). |  | $A_1$ (R heads). |  |
|---|---|---|---|---|---|---|---|---|---|
|  | λ. | $\nu_{vac.}$ | λ. | $\nu_{vac.}$ |  | λ. | $\nu_{vac.}$ | λ. | $\nu_{vac.}$ |
| 0, 0 | — | — | — | — | 1, 0 | — | — | 3646·29 | 27417·16 |
| 1, 1 | — | — | 3712·36 | 26929·35 | 2, 1 | — | — | 52·17 | 373·03 |
| 2, 2 | — | — | 18·02 | 888·45 | 3, 2 | 3660·66 | 27309·72 | 58·01 | 329·27 |
| 3, 3 | — | — | 23·60 | 848·09 | 4, 3 | 66·64 | 265·20 | 63·82 | 285·95 |
| 4, 4 | — | — | 29·16 | 808·14 | 5, 4 | 72·63 | 220·73 | 69·59 | 243·06 |
| 5, 5 | 3738·65 | 26740·04 | 34·66 | 768·60 | 6, 5 | 78·59 | 176·65 | 75·27 | 200·96 |
| 6, 6 | 44·31 | 699·63 | 40·02 | 730·32 | 7, 6 | 84·54 | 132·70 | 80·97 | 158·85 |
| 7, 7 | 49·88 | 659·99 | 45·56 | 690·66 | 8, 7 | 90·42 | 089·48 | 86·56 | 117·62 |
| 8, 8 | *55·58 | 619·46 | 50·98 | 652·17 | 9, 8 | 96·26 | 046·69 | 92·13 | 076·79 |
| 9, 9 | 60·81 | 582·52 | — | — | 10, 9 | †3702·15 | 003·67 | 97·70 | 035·95 |
| 10, 10 | 65·99 | 545·90 | 61·96 | 576·45 | 11, 10 | — | — | 3703·12 | 26996·38 |
| 11, 11 | 71·09 | 510·08 | 66·93 | 539·28 |  |  |  |  |  |
| 12, 12 | 76·14 | 474·57 | 72·0 | 503·62 |  |  |  |  |  |
| 13, 13 | 81·07 | 440·06 | 77·29 | 466·51 |  |  |  |  |  |
| 14, 14 | 85·79 | 406·34 | 82·44 | 430·48 |  |  |  |  |  |
| 15, 15 | 90·71 | 372·84 | 87·75 | 393·37 |  |  |  |  |  |
| 16, 16 | †95·55 | 339·22 | 92·93 | 357·41 |  |  |  |  |  |

* Value smoothed before computation.
† Value omitted in computation.

The ultra-violet system presents considerable difficulty in the matter of an accurate assignment of vibrational quantum numbers. This arises from the weakness of the system, and the resulting absence of several of the leading members. In making the assignment of Table VI the following considerations have been weighed. We are probably dealing with a (1, 0) and a (0, 0) sequence as is certainly the case in the similar system $A_4'A_3'$. A final state in common with the latter system is indicated, but, as in the similar case of CaF, there is a remarkable discrepancy in the coefficients of $n''^2$ in the two cases. An assignment of $n''$ has therefore been made in such a way as to bring $\omega_0\,(= a)$, the coefficient of $n''$ into approximate agreement. The $n'$ and $n''$ values of the $A_2'$ and $A_1'$ sequences could each be reduced by unity without greatly affecting $a'$ and $a''$, but this would result in an increase of the Q–R interval from 20–30 ν to 60–70 ν, and this is not the simplest or most reasonable assumption. On the basis of the assignment made, the leading R head of the $A_2$ (0, 0) sequence has not been recorded by Datta. [*]Walters and Barratt record the

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[*] The authors have kindly informed me that where the presence of an absorption band was doubtful, it has been invariably omitted from their tables.

(1,0) band at $\nu$. 27417 faintly in absorption; the predicted (0, 0) band at $\nu$. 26961 was doubtless too faint for observation. Accepting the assignment of Table VI we have found expressions for $A_2'$ and $A_1'$ by the method of Least Squares, viz.:—

$$(A_2')\quad \nu = 26960{\cdot}821 - 47{\cdot}0996n'' + 0{\cdot}63157n''^2 - 0{\cdot}006944n''^3$$
$$(A_1')\quad \nu = 27398{\cdot}686 - 44{\cdot}3219n'' - 0{\cdot}11952n''^2 + 0{\cdot}020000n''^3$$

which give by equation (10):—

$$a' = 437{\cdot}095 \quad b' = -1{\cdot}0133 \quad c' = -0{\cdot}25036$$
$$a'' = 484{\cdot}195 \quad b'' = -0{\cdot}3817 \quad c'' = -\begin{cases} 0{\cdot}24342\ (A_2') \\ 0{\cdot}27036\ (A_1') \end{cases}$$

While these express the two sequences very well it will be observed (1) that $a''$ is decidedly different from that given by equations (18), (19) and (20); (2) that the coefficients of the terms in $n'^2$ and $n''^2$ are *positive*, which is impossible for a stable anharmonic oscillator; and (3) that the coefficients of the cubic terms are unusually large.

These features all arise from the sparseness of the data given by Datta, especially near the origin of the system, and from the fact that the recorded positions of some of the heads are of doubtful accuracy. Using, therefore, a quadratic formula to express the sequences, we find

$$(A_2')\quad \nu = 26955{\cdot}113 - 45{\cdot}140n'' + 0{\cdot}42325n''^2$$
$$(A_1')\quad \nu = 27400{\cdot}485 - 45{\cdot}682n'' + 0{\cdot}18048n''^2,$$

and from these we obtain:—

$$\left.\begin{array}{lll} & a' = 445{\cdot}643 & b' = +0{\cdot}271 \\ \nu_e = 26955{\cdot}11 & & \\ & a'' = 490{\cdot}783 & b'' = \begin{cases} +0{\cdot}694\ (A_2') \\ +0{\cdot}451\ (A_1') \end{cases} \end{array}\right\} \qquad (17)$$

This value of $a''$ is in better agreement with that of equations (18), (19) and (20), and the values of $b'$ and $b''$ are positive (so that the coefficients of $n'^2$ and $n''^2$ are negative). There is still, however, a large discrepancy between the values of $b''$ of equations (17), and say, (18). This feature, which also occurs in the analogous system of CaF, must be left for the present unexplained. Any attempt to increase the values of ($n'$, $n''$) to effect better agreement of $a''$ in (17) with $a''$ of (18) and (19) will conflict with the absorption data of Walters and Barratt, and also lead quickly to negative values of $b'$ and $b''$.

In Table VII is given the experimental data of the $2\,^2S \rightarrow 1\,^2S$ system in the

Table VII.

$2\,{}^2S \rightarrow 1\,{}^2S$.

| $n', n''$. | Int. | $A_4'$ (Q heads). | | Int. | $A_4$ (R heads). | | $n', n''$. | Int. | $A_3'$ (Q heads). | | Int. | $A_3$ (R heads). | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | λ. | $\nu_{vac.}$ | | λ. | $\nu_{vac.}$ | | | λ. | $\nu_{vac.}$ | | λ. | $\nu_{vac.}$ |
| 0, 0 | 10 | 5779·446 | 17297·91 | 8 | 5771·97 | 17320·32 | 1, 0 | 0 | 5621·77 | 17783·07 | — | — | — |
| 1, 1 | 9 | 82·12 | 89·91 | 8 | 74·775 | 11·90 | 2, 1 | 1 | 25·52 | 71·21 | — | — | — |
| 2, 2 | 8 | 84·834 | 81·80 | 8 | 77·626 | 03·36 | 3, 2 | 2 | 29·24 | 59·47 | 1 | 5625·52 | 17771·21 |
| 3, 3 | 8 | 87·576 | 73·61 | 6 | 80·517 | 17294·70 | 4, 3 | 3c | 32·99 | 47·65 | 2 | 29·24 | 59·47 |
| 4, 4 | 8 | 90·34 | 65·37 | 5 | 83·422 | 86·02 | 5, 4 | 4 | 36·90 | 35·34 | 3c | 32·99 | 47·65 |
| 5, 5 | 8 | 93·14 | 57·02 | 5 | 86·36 | 77·24 | 6, 5 | 4 | 40·775 | 23·15 | 4 | 36·71 | 35·93 |
| 6, 6 | 8 | 95·98 | 48·56 | 5 | 89·335 | 68·36 | 7, 6 | 4 | 44·68 | 10·89 | 4 | 40·51 | 23·98 |
| 7, 7 | 7 | 98·87 | 39·97 | 4 | 92·36 | 59·34 | 8, 7 | 4 | 48·62 | 17698·54 | 4 | 44·344 | 11·95 |
| 8, 8 | 7 | 5801·796 | 31·28 | 3c | 95·41 | 50·26 | 9, 8 | 4c | 52·60 | 86·08 | 4 | 48·21 | 17699·82 |
| 9, 9 | 7c | 04·68 | 22·72 | 3 | 98·50 | 41·07 | 10, 9 | 3 | 56·60 | 73·57 | 4c | 52·11 | 87·61 |
| 10, 10 | 7c | 07·70 | 13·76 | 1 | 5801·64 | 31·74 | 11, 10 | 3 | 60·67 | 60·87 | 3 | 56·044 | 75·31 |
| 11, 11 | 6c | 10·617 | 05·12 | — | — | — | 12, 11 | 3 | 64·72 | 48·24 | 3 | 60·01 | 62·92 |
| 12, 12 | 6 | 13·693 | 17196·01 | — | — | — | 13, 12 | 2 | 68·80 | 35·53 | 3 | 64·014 | 50·44 |
| 13, 13 | 6 | 16·74 | 87·01 | — | — | — | 14, 13 | 2 | 72·93 | 22·70 | 2 | 68·036 | 38·91 |
| 14, 14 | 5 | *19·96 | 77·50 | 2? | 14·17 | 17194·60 | 15, 14 | 2c | 77·08 | 09·81 | 2c | 72·12 | 25·21 |
| 15, 15 | 5 | 23·02 | 68·47 | 2 | 17·43 | 84·97 | 16, 15 | ? | †81·3 | 17596·7 | 2c | 76·23 | 12·45 |
| 16, 16 | 4c | *26·08 | 59·45 | 1 | 20·78 | 75·08 | 17, 16 | — | — | — | 1c | 80·38 | 17599·59 |
| 17, 17 | 4 | 29·40 | 49·68 | 1 | 24·045 | 65·45 | 18, 17 | — | — | — | — | — | — |
| 18, 18 | 4 | 32·74 | 39·86 | 1c | 27·285 | 55·90 | 19, 18 | — | — | — | — | — | — |
| 19, 19 | 4 | 35·975 | 30·36 | 1c | 30·62 | 46·09 | 20, 19 | 1 | 98·4 | 43·9 | — | — | — |
| 20, 20 | 3 | 39·26 | 20·72 | 2c | 34·07 | 35·95 | 21, 20 | — | — | — | 1 | 97·19 | 47·65 |
| 21, 21 | 2 | 42·60 | 10·93 | | | | 22, 21 | 0c | 5707·05 | 17·34 | — | — | — |
| 22, 22 | 2c | 46·00 | 00·98 | | | | 23, 22 | 0 | 11·49 | 03·72 | 1c | 5705·74 | 21·36 |
| 23, 23 | 2c | 49·39 | 17091·07 | | | | 24, 23 | — | — | — | 0 | 10·14 | 07·86 |
| 24, 24 | 1c | 52·92 | 80·77 | | | | 25, 24 | 0 | 20·37 | 17476·55 | — | — | — |
| | | | | | | | 26, 25 | — | — | — | 0 | 18·84 | 17481·23 |

* Value smoothed before computation.

† From this downwards the data was not used in computation.

yellow-green region of the spectrum. The (1, 0) sequence has a peculiar appearance, the leading members being apparently single, while doublets of increasing separation appear as we pass to the higher members. It is seen to arise from the fact that the R head of each band falls approximately on the Q head of the preceding band, and this superposition is very precise at the beginning of the sequence.

Applying the preceding methods to the system we find :—

$$(A_4') \quad \nu = 17297\cdot875 - \phantom{1}7\cdot9567n'' - 0\cdot04396n''^2 - 0\cdot000057n''^3$$

$$(A_3') \quad \nu = 17783\cdot046 - 11\cdot6731n'' - 0\cdot06411n''^2 + 0\cdot001013n''^3,$$

and hence by equation (10) :—

$$\left.\begin{array}{l} \qquad\qquad\qquad a' = 487\cdot046 \quad b' = 1\cdot8683 \quad c' = \quad -0\cdot00672 \\ \nu_e = 17297\cdot87 \\ \qquad\qquad\qquad a'' = 495\cdot003 \quad b'' = 1\cdot8243 \quad c'' = \begin{cases} -0\cdot00666\ (A_4') \\ -0\cdot00773\ (A_3') \end{cases} \end{array}\right\} . \qquad (18)$$

The one notable feature is that (as in CaF), $a' < a''$ but $b' > b''$, a circumstance which causes a *divergence* of successive members in the case of both sequences. The (0, 0) band of the system, as would be expected, is found strongly in absorption.

We turn finally to the most complex of the three systems, viz., that in the orange-red region, which arises from the electronic transition $2\,^2P \rightarrow 1\,^2S$. The data are in Table VIII. The system is on the whole better developed than its analogue in CaF. This is particularly notable in the case of the (1, 0) sequences $B_1$ and $B_3$, which attain considerable strength. (The $B_2$ heads are presumably P heads associated with the Q heads of the $B_1$ sequence, but the assignment of vibrational quantum numbers to it is a little uncertain.) It will be recalled that in CaF the analogue of $B_3$ was unrecorded. While the ($n'$, $n''$) assignment of $C_3$ and $C_4$ (the Q heads) is reasonably certain, that of $C_3'$ and $C_4'$ is possibly in error owing to the absence of leading members from the experimental data. There is also no definite guidance available as to the magnitude of the expected P–Q separation. While for the (0, 0) sequences associated with the two $^2P$ levels these are approximately 36 and 52 $\nu$, it is impossible to say whether their magnitude or even their ratio should be found also in the (0, 1) sequence. Assuming the same ratio to be roughly preserved, the appropriate assignment of $C_3'$ and $C_4'$ has been made in Table VIII. Possibly, however, the ($n'$, $n''$) values of all these P heads should be increased by unity, thus moving them down the table one place. This same ambiguity

Table VIII.

$(2\,^2P_1 \rightarrow 1\,^2S)$ ? $2\,^2P \rightarrow 1\,^2S$. $(2\,^2P_2 \rightarrow 1\,^2S)$ ?

| $n', n''$. | Int. | $B_1$ (Q heads). | | Int. | $B_2$ (P heads). | | $n', n''$. | Int. | $B_3$ (Q heads). | | Int. | (P heads). | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | λ. | $\nu_{vac.}$ | | λ. | $\nu_{vac.}$ | | | λ. | $\nu_{vac.}$ | | λ. | $\nu_{vac.}$ |
| 1, 0 | 8 | 6306·07 | 15853·36 | 1 | 6332·25 | 15787·82 | 1, 0 | 6 | 6419·01 | 15574·43 | | | |
| 2, 1 | 9 | 04·75 | 56·68 | 1 | 30·89 | 91·21 | 2, 1 | 8 | 17·74 | 77·51 | | | |
| 3, 2 | 9 | 03·48 | 59·88 | 2 | 29·55 | 94·55 | 3, 2 | 8 | 16·487 | 80·56 | | | |
| 4, 3 | 9 | 02·21 | 63·07 | 2 | 28·25 | 97·80 | 4, 3 | 8 | 15·27 | 83·51 | | | |
| 5, 4 | 9 | 00·99 | 66·14 | 3 | 27·01 | 15800·91 | 5, 4 | 8 | 14·10 | 86·35 | | | |
| 6, 5 | 8 | 6299·79 | 69·16 | 3 | 25·85 | 03·79 | 6, 5 | 7 | 12·95 | 89·15 | | | |
| 7, 6 | 8 | 98·65 | 72·04 | 3 | 24·67 | 06·74 | 7, 6 | 6 | 11·81 | 91·92 | | | |
| 8, 7 | 8 | 97·51 | 74·91 | 2 | 23·63 | 09·34 | 8, 7 | 5 | 10·73 | 94·55 | | | |
| 9, 8 | 8 | 96·46 | 77·56 | ? | 22·67 | 11·74 | 9, 8 | 4 | 09·68 | 97·10 | | | |
| 10, 9 | 7 | 95·40 | 80·23 | | | | 10, 9 | ? | — | (99·59) | | | |
| 11, 10 | 7 | 94·39 | 82·78 | | | | 11, 10 | 3 | 07·66 | 15602·02 | | | |
| 12, 11 | 7 | 93·43 | 85·20 | | | | 12, 11 | 4 | 06·69 | 04·38 | | | |
| 13, 12 | 6 | 92·48 | 87·60 | | | | 13, 12 | 3 | 05·75 | 06·67 | | | |
| 14, 13 | 6 | 91·61 | 89·80 | | | | 14, 13 | 2 | 04·87 | 08·82 | | | |
| 15, 14 | 6 | 90·74 | 91·99 | | | | 15, 14 | 2 | 04·00 | 10·93 | | | |
| 16, 15 | 5 | 89·95 | 93·99 | | | | 16, 15 | 2 | 03·18 | 12·94 | | | |
| 17, 16 | 5 | 89·19 | 95·91 | | | | 17, 16 | 2 | 02·39 | 14·86 | | | |
| 18, 17 | 4 | 88·44 | 97·81 | | | | 18, 17 | 1 | 01·66 | 16·64 | | | |
| 19, 18 | 3 | 87·77 | 99·50 | | | | 19, 18 | 1 | 00·93 | 18·42 | | | |
| 20, 19 | 2 | 87·10 | 15901·20 | | | | 20, 19 | — | — | — | | | |
| 21, 20 | 2 | 86·51 | 02·69 | | | | 21, 20 | 1 | 6399·64 | 21·57 | | | |
| 22, 21 | 1 | 85·95 | 04·10 | | | | 22, 21 | 1 | 99·01 | 23·11 | | | |
| 23, 22 | 1 | 85·485 | 05·28 | | | | Tail | 3 | 94·7 | 33·6 | | | |
| 24, 23 | 0 | 85·06 | 06·35 | | | | | | | | | | |
| Tail | 4 | 83·13 | 11·24 | | | | | | | | | | |

Table VIII—(continued).

| $n', n''$. | Int. | $C_1$ (Q heads). | | Int. | $C_1'$ (P heads). | | $n', n''$. | Int. | $C_2$ (Q heads). | | Int. | $C_2'$ (P heads). | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | λ. | $\nu_{vac.}$ | | λ. | $\nu_{vac.}$ | | | λ. | $\nu_{vac.}$ | | λ. | $\nu_{vac.}$ |
| 0, 0 | 15 | 6512·037 | 15351·95 | 10 | 6527·63 | 15315·27 | 0, 0 | 15 | 6632·666 | 15072·74 | 8 | 6655·58 | 15020·85 |
| 1, 1 | 10 | 08·73 | 59·74 | 9 | 24·203 | 23·32 | 1, 1 | 13 | 29·372 | 80·23 | 8 | 52·13 | 28·64 |
| 2, 2 | 8 | 05·46 | 67·47 | 8 | 20·835 | 31·23 | 2, 2 | 11 | 26·11 | 87·65 | 8 | 48·72 | 36·34 |
| 3, 3 | 7 | 02·235 | 75·09 | 8 | 17·527 | 39·01 | 3, 3 | 10 | 22·917 | 94·93 | 7 | 45·37 | 43·92 |
| 4, 4 | 7 | 6499·01 | 82·72 | 7 | 14·243 | 46·75 | 4, 4 | 9 | 19·761 | 15102·12 | 6 | 42·04 | 51·46 |
| 5, 5 | 5c | †95·98 | 89·89 | 5 | 11·11 | 54·13 | 5, 5 | 8c | †16·58 | 09·38 | 5 | 38·83 | 58·74 |
| 6, 6 | 5c | 92·88 | 97·23 | 4c | 07·89 | 61·73 | 6, 6 | 7 | 13·58 | 16·24 | 5 | 35·61 | 66·05 |
| 7, 7 | 4c | 89·87 | 15404·38 | | | | 7, 7 | 6 | 10·52 | 23·19 | | | |
| 8, 8 | 4c | 86·97 | 11·27 | | | | 8, 8 | 5 | 07·59 | 29·94 | | | |
| 9, 9 | 3 | 84·01 | 18·30 | | | | 9, 9 | 5c | *04·60 | 36·79 | | | |
| 10, 10 | 2 | 81·24 | 24·89 | | | | 10, 10 | 4c | *01·82 | 43·16 | | | |
| 11, 11 | 1 | 78·46 | 31·51 | | | | | | | | | | |
| 12, 12 | 1c | 75·86 | 37·71 | | | | | | | | | | |

Table VIII—(continued).

| $n', n''$. | Int. | $C_3$ (Q heads). | | Int. | $C_3'$ (P heads). | | $n', n''$. | Int. | $C_4$ (Q heads). | | Int. | $C_4'$ (P heads). | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | λ. | $\nu_{vac.}$ | | λ. | $\nu_{vac.}$ | | | λ. | $\nu_{vac.}$ | | λ. | $\nu_{vac.}$ |
| 0, 1 | 4 | §6729·42 | 14856·03 | 0 | §6740·98 | 14830·55 | 0, 1 | — | 6858·695 | 14576·02 | — | — | — |
| 1, 2 | 2 | §24·01 | 67·98 | 1 | §35·40 | 42·84 | 1, 2 | — | 53·13 | 87·85 | — | 6869·405 | 14553·29 |
| 2, 3 | 3? | §18·57 | 80·02 | — | 29·89 | 55·00 | 2, 3 | 1*c* | §47·55 | 99·74 | — | 63·72 | 65·36 |
| 3, 4 | — | 13·25 | 91·81 | — | 24·43 | 67·05 | 3, 4 | 2*c* | 42·195 | 14611·17 | — | 58·215 | 77·04 |
| 4, 5 | — | 08·03 | 14903·41 | 2 | 19·06 | 78·93 | 4, 5 | 2*c* | 36·795 | 22·71 | — | 53·13 | 87·85 |
| 5, 6 | — | 02·78 | 15·08 | — | 13·75 | 90·70 | 5, 6 | 2*c* | 31·48 | 34·08 | 1*c* | 47·59 | 99·66 |
| 6, 7 | — | 6697·57 | 26·67 | — | 08·57 | 14902·21 | 6, 7 | — | 26·37 | 45·04 | 2*c* | 42·19 | 14611·17 |
| 7, 8 | — | 92·42 | 38·16 | — | 03·42 | 13·64 | 7, 8 | 1*c* | 21·18 | 56·19 | 2*c* | 36·79 | 22·71 |
| 8, 9 | — | 87·39 | 49·40 | — | 6698·375 | 24·88 | 8, 9 | 1*c* | †16·395 | 66·47 | 2*c* | 31·48 | 34·08 |
| 9, 10 | — | — | — | — | 93·33 | 36·13 | 9, 10 | — | †11·74 | 76·50 | — | 26·37 | 45·04 |
| 10, 11 | — | — | — | — | 88·30 | 47·36 | 10, 11 | — | †06·60 | 87·57 | 1*c* | 21·18 | 56·19 |
| 11, 12 | — | — | — | — | 83·44 | 58·24 | 11, 12 | — | 01·15 | 99·34 | 1*c* | 16·395 | 66·47 |
| | | | | | | | 12, 13 | — | 6796·545 | 14709·30 | — | 11·17 | 77·73 |
| | | | | | | | 13, 14 | — | — | (719·7) | — | 06·18 | 88·48 |
| | | | | | | | 14, 15 | — | †86·73 | 30·57 | — | 01·15 | 99·34 |
| | | | | | | | 15, 16 | — | 82·535 | 39·69 | — | 6795·90 | 14710·70 |
| | | | | | | | 16, 17 | — | 78·11 | 49·31 | — | — | — |
| | | | | | | | 17, 18 | — | 73·62 | 59·09 | — | 86·73 | 30·57 |
| | | | | | | | 18, 19 | — | — | — | — | 82·53 | 39·69 |

* Value omitted on computation.

† Value smoothed before computation.

§ Johnson's value. The remaining data in $C_3$, $C_3'$, $C_4$, $C_4'$ are Leopold's.

was found in Table IV. Using the previous methods, we find the various sequences are given by :—

$$(\mathrm{B}_1) \quad \nu = 15853{\cdot}365 + 3{\cdot}3482n'' - 0{\cdot}03726n''^2 - 0{\cdot}000348n''^3$$

$$(\mathrm{C}_1) \quad \nu = 15351{\cdot}940 + 7{\cdot}8674n'' - 0{\cdot}04485n''^2 - 0{\cdot}001227n''^3,$$

and from these we obtain :—

$$\nu_e = 15351{\cdot}94 \quad \left.\begin{array}{llll} a' = 503{\cdot}678 & b' = 2{\cdot}2558 & c' = & +\,0{\cdot}00253 \\ a'' = 495{\cdot}811 & b'' = 2{\cdot}2110 & c'' = & \begin{cases} +\,0{\cdot}00376\ (\mathrm{C}_1) \\ +\,0{\cdot}00288\ (\mathrm{B}_1) \end{cases} \end{array}\right\}. \qquad (19)$$

Using the sequences $\mathrm{B}_3$ and $\mathrm{C}_2$ associated with the lower level of the $^2\mathrm{P}$ state, we have :—

$$(\mathrm{B}_3) \quad \nu = 15574{\cdot}442 + 3{\cdot}1161n'' - 0{\cdot}03336n''^2 - 0{\cdot}000224,$$

$$(\mathrm{C}_2) \quad \nu = 15072{\cdot}744 + 7{\cdot}5346n'' - 0{\cdot}04533n''^2 - 0{\cdot}000320,$$

and from these :—

$$\nu_e = 15072{\cdot}74 \quad \left.\begin{array}{llll} a' = 503{\cdot}897 & b' = 2{\cdot}2032 & c' = & +0{\cdot}00399 \\ a'' = 496{\cdot}363 & b'' = 2{\cdot}1579 & c'' = & \begin{cases} +\,0{\cdot}00431\ (\mathrm{C}_2) \\ +\,0{\cdot}00453\ (\mathrm{B}_3) \end{cases} \end{array}\right\}. \qquad (20)$$

Substituting the data of equation (19) in (13) we can predict the $\mathrm{C}_3$ (1, 0) sequence, and similarly using the data of (20) we can predict $\mathrm{C}_4$. These predicted formulæ are given below, together with the Least Squares' formulæ derived from the experimental date.

$$(\mathrm{C}_3) \begin{cases} (\text{Pred.}) \quad \nu = 14846{\cdot}004 + 12{\cdot}3866n'' - 0{\cdot}05244n''^2 - \begin{Bmatrix} 0{\cdot}001227 \\ 0{\cdot}000348 \end{Bmatrix} n''^3 \\ (\text{Obs.}) \quad \nu = 14843{\cdot}918 + 12{\cdot}1530n'' - 0{\cdot}04794n''^2 + 0{\cdot}000034n''^3 \end{cases}$$

$$(\mathrm{C}_4) \begin{cases} (\text{Pred.}) \quad \nu = 14566{\cdot}640 + 11{\cdot}9531n'' - 0{\cdot}05730n''^2 - \begin{Bmatrix} 0{\cdot}000320 \\ 0{\cdot}000224 \end{Bmatrix} n''^3 \\ (\text{Obs.}) \quad \nu = 14564{\cdot}076 + 12{\cdot}0305n'' - 0{\cdot}06057n''^2 - 0{\cdot}000339n''^3 \end{cases}$$

In Table IX are summarised data relating to the various levels of the SrF molecule. In the case of the normal level 1 $^2\mathrm{S}$, the mean value of the constants from (19) and (20) has been given, but for specific purposes the precise values of (17) to (20) must be used. The difference in the values of $a''$ and $b''$ (especially of the latter) as given in (18) and either (19) or (20) is remarkable. The same genuine discrepancy was found for the analogous CaF systems, and, as

Table IX.

| Level. | Energy. | | $a$ $(\omega_0)$. | $b$ $(\omega_0 x)$. | $c$. |
|---|---|---|---|---|---|
| | $\nu$. | Volts. | | | |
| $1\,^2S$ | 0 | 0 | 496·087 | 2·184 | +0·0038 |
| $2\,^2P_2$ } | 15072·74 | 1·861 | 503·897 | 2·2032 | +0·00399 |
| $2\,^2P_1$ } | 15351·94 | 1·895 | 503·678 | 2·2558 | +0·00253 |
| $2\,^2S$ | 17297·87 | 2·135 | 487·046 | 1·8683 | −0·00672 |
| $3\,^2S$ (?) | 26955·11 | 3·327 | 445·643 | 0·271 | — |

mentioned there, it probably corresponds to some fundamental peculiarity in the S states of all the alkaline earth fluorides. Fig. 3 gives a survey of the energy levels of the SrF molecule. As in fig. 1, the broken lines are vibrational levels. The transitions corresponding to the leading member of each sequence have been marked.

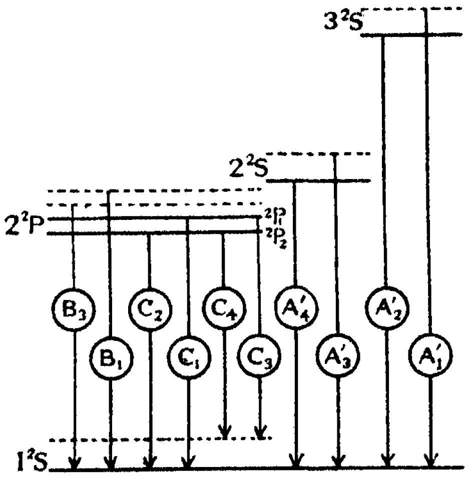

FIG. 3.—Energy Levels of the SrF Molecule.

The various systems do not supply very consistent values of the energy of dissociation of the molecule. It is believed, however, to be somewhere in the neighbourhood of 27000 ν. It is at least of the same order as that required for dissociation of the CaF molecule.

## *Summary.*

(1) A complete quantum analysis of the whole of the band spectra of the molecules CaF and SrF has been made. Formulæ which express them have

been obtained by the Method of Least Squares. For this purpose a re-measurement of some 250 band heads has been made from first order plates taken on a 21-foot Rowland grating.

(2) The molecules each give rise to at least three band systems which are analogous in almost every respect. These are assigned to the electron transitions 3 $^2S \rightarrow 1\,^2S$, 2 $^2S \rightarrow 1\,^2S$, and 2 $^2P \rightarrow 1\,^2S$.

(3) While as regards types of transition, etc., these molecules have features common to all those of the one-valence electron type, there exist several exceptional features. Among these may be mentioned (*a*) the occurrence of strong Q branches in $^2S \rightarrow {}^2S$ transitions, and (*b*) a definite discrepancy in ($n''$) as evaluated from the $^2S \rightarrow {}^2S$ and $^2P \rightarrow {}^2S$ systems. These points to some unusual feature in the $^2S$ states of all these molecules.

(4) The appearance of these band systems is of an unusual character, characterised by very long sequences in which the members are close together. Only the sequences $\Delta n = 0$, and $\pm 1$ occur. These features are explained in terms of the smallness of the change in the vibrational constants with change of electronic state.

(5) There is a characteristic "tail" formation associated with many of the band sequences, and this has been shown to accord with theoretical expectations.

(6) The energy of dissociation of the CaF molecule is approximately 27200 . ν (= 3·36 volts), and that of SrF is of the same order. In the case of the former molecule the sudden termination of a sequence ($B_1$) at the 20th member has been satisfactorily explained on the basis of this value for the energy of dissociation.

# *The Band Spectra of the Alkaline Earth Halides.* II.—BaF, MgF.

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## *Introduction.*

In a previous paper[*] an analysis of the gross structure of the band spectra of the CaF and SrF molecules has been made. We shall here deal with the spectra of two molecules of precisely the same external character, but one of which is simpler and the other more complex in its internal structure. MgF has one shell of eight electrons *less* than CaF, the other molecule BaF has a shell of 18 electrons *more* than SrF.

The barium fluoride bands can be produced in the flame or arc, and, using the latter source, George[†] measured these from spectrograms taken on a 21-foot grating. For purposes of analysis and the resolution of several doubtful points it was found necessary to obtain new measurements, and Tables I and II present the data obtained from several first order plates of very good definition taken on a 21-foot Rowland grating.

Under similar conditions of excitation the magnesium fluoride bands can be produced, but they are intrinsically fainter and much longer exposures are necessary. The first good measurements of these bands appear to be those of Datta,[‡] and for purposes of this communication his experimental data have been used. For convenience Datta's designation of the various sequences by letters, A, B, C, D, E, etc., has been retained, and reference may be made to his paper for an excellent plate of reproductions of these bands.

Mecke[§], alone, has worked on these band spectra from the modern theoretical standpoint. He has obtained and analysed one system in the case of each molecule, and has traced the general changes in these spectra as we pass along the series of molecules BeF, MgF, CaF, SrF, BaF. The present paper amplifies and extends the analysis of these spectra so as to include all the known bands. These results have further been examined in the light of Walters and Barratt's data[||] on the absorption spectra of these molecules.

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[*] *Supra*, p. 161.

[†] 'Z. Wiss. Photogr.,' vol. 12, p. 254 (1913).

[‡] 'Roy. Soc. Proc.,' A, vol. 99, p. 436 (1921).

[§] 'Z. Physik,' vol. 42, p. 390 (1927).

[||] 'Roy. Soc. Proc.,' A, vol. 118, p. 120 (1928).

### *The Band Spectra of* BaF.

The familiar bands of barium fluoride occur in the green region of the spectrum, and are degraded to the red side. The characteristic groups of bands are " sequences " (distinguished by $\Delta n =$ constant). In their prolonged and compact nature, and in the circumstance that only one or possibly two sequences go to compose a complete system, they obviously present features in common with groups in CaF and SrF spectra. The sequences fall into two systems, and they have been arranged as such in Tables I and II. It is believed that the first system corresponds to the transition $2\,{}^2S \rightarrow 1\,{}^2S$. $C_1'$ and $B_3$ are respectively the (0, 0) and (0, 1) sequences of Q heads; $C_1$ constitutes R heads associated with $C_1'$, and George's faint group E[*] (beginning at $\lambda$ 5102·67) are believed to be the R heads associated with $B_3$. The leading members of the $B_3$ (0, 1) sequence have only been observed with vanishingly small intensity, and for this reason there would appear to be a possibility of error in the assignment of $(n', n'')$. The agreement of the vibrational structure of the final electronic state with that derived from another system (which will be considered later) is, however, good reason for supposing the $(n', n'')$ values given to $B_3$ to be correct. If

$$\nu = \nu_e + (a'n' - b'n'^2 + c'n'^3) - (a''n'' - b''n''^2 + c''n''^3)$$

represents a band system, the (1, 0), (0, 0), and (0, 1) sequences are given by

$$\left.\begin{aligned}
&(1, 0) \quad \nu = \nu_e + a' - b' + c' + (a' - a'' - 2b' - 3c')\,n'' \\
&\qquad\qquad\qquad - (b' - b'' - 3c')\,n''^2 + (c' - c'')\,n''^3 \\
&(0, 0) \quad \nu = \nu_e + (a' - a'')\,n'' - (b' - b'')\,n'' + (c' - c'')\,n''^3 \\
&(0, 1) \quad \nu = \nu_e - a' - b' - c' + (a' - a'' + 2b' + 3c')\,n'' \\
&\qquad\qquad\qquad - (b' - b'' + 3c')\,n''^2 + (c' - c'')n''^3
\end{aligned}\right\}. \qquad (1)$$

The method adopted, as in a previous paper, has been to express the sequences by cubic formulæ, and determine the vibrational constants by equation (1). Using the method of Least Squares we have thus found :

$$(C_1') \quad \nu = 19991{\cdot}975 - 12{\cdot}1805n'' + 0{\cdot}15510n''^2 - 0{\cdot}000762n''^3$$

$$(B_3) \quad \nu = 19537{\cdot}620 - 8{\cdot}3800n'' + 0{\cdot}10802n''^2 + 0{\cdot}002185n''^3$$

and from these we obtain :

$$\left.\begin{array}{ll}
 & a' = 452{\cdot}464 \quad b' = 1{\cdot}8767 \quad c' = +\,0{\cdot}01569 \\
\nu_e = 19991{\cdot}975 & \\
 & a'' = 464{\cdot}644 \quad b'' = 2{\cdot}0318 \quad c'' = +\left\{\begin{array}{l} 0{\cdot}01645\ (C_1') \\ 0{\cdot}01351\ (B_3) \end{array}\right.
\end{array}\right\}. \qquad (2)$$

---

[*] Datta (*loc. cit.*, p. 447) has made several mistakes in referring to these groups. On line 4 he means " the group designated as E by George." This is a faint group of five recorded heads. Again, in Table VIII, p. 447, Datta's $B_3$ is George's group D.

Table I.

$2\,^2S \rightarrow 1\,^2S$.

| $n', n''$. | Int. | $C_1'$ (Q heads). |  | Int. | $C_1$ ( R heads). |  | $n', n''$. | Int. | $B_3$ (Q heads). |  | Int. | *(R heads). |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | λ. | $\nu_{vac.}$ |  | λ. | $\nu_{vac.}$ |  |  | λ. | $\nu_{vac.}$ |  | λ. | $\nu_{vac.}$ |
| 0, 0 | 7 | 5000·615 | 19991·98 | 6 | 4992·096 | 20026·10 | 0, 1 | 00 | 5119·06 | 19529·41 | — | 5102·67 | 19592·14 |
| 1, 1 | 6 | 03·630 | 79·97 | 5 | 94·943 | 15·68 | 1, 2 | 0 | 21·21 | 21·21 | — | 04·74 | 84·20 |
| 2, 2 | 5 | 06·572 | 68·19 | 4 | 97·718 | 03·57 | 2, 3 | 1 | 23·254 | 13·42 | — | 06·59 | 77·10 |
| 3, 3 | 5 | 09·421 | 56·84 | 3 | 5000·450 | 19992·64 | 3, 4 | 1 | 25·115 | 06·34 | — | 08·19 | 70·97 |
| 4, 4 | 4 | 12·235 | 45·63 | 1 | 03·065 | 82·19 | 4, 5 | 2 | 27·174 | 19498·51 | — | 09·58 | 65·64 |
| 5, 5 | 4 | 14·94 | 34·87 | — | — | — | 5, 6 | 1c | 29·01 | 91·53 |  |  |  |
| 6, 6 | 3 | 17·591 | 24·34 | 1 | 08·09 | 62·14 | 6, 7 | 1c | 30·75 | 84·91 |  |  |  |
| 7, 7 | 2 | 20·173 | 14·09 | 0 | 10·54 | 52·38 | 7, 8 | 2 | 32·38 | 78·73 |  |  |  |
| 8, 8 | 2 | 22·72 | 03·99 | 0 | 12·89 | 43·02 | 8, 9 | 2 | 33·99 | 72·62 |  |  |  |
| 9, 9 | 2 | 25·137 | 19894·42 |  |  |  | 9, 10 | 2 | 35·51 | 66·85 |  |  |  |
| 10, 10 | 2 | 27·540 | 84·91 |  |  |  | 10, 11 | 1 | 36·95 | 61·40 |  |  |  |
| 11, 11 | 2 | 29·865 | 75·72 |  |  |  | 11, 12 | 0 | 38·22 | 56·59 |  |  |  |
| 12, 12 | 1 | 32·147 | 66·71 |  |  |  |  |  |  |  |  |  |  |
| 13, 13 | 1 | 34·299 | 58·22 |  |  |  |  |  |  |  |  |  |  |
| 14, 14 | 1 | 36·419 | 49·86 |  |  |  |  |  |  |  |  |  |  |
| 15, 15 | 0 | 38·5 | 41·66 |  |  |  |  |  |  |  |  |  |  |
| 16, 16 | 0 | 40·53 | 33·67 |  |  |  |  |  |  |  |  |  |  |
| 17, 17 | 0 | 42·51 | 25·88 |  |  |  |  |  |  |  |  |  |  |
| 18, 18 | 0 | 44·39 | 18·42 |  |  |  |  |  |  |  |  |  |  |
| 19, 19 | 0 | 46·19 | 11·42 |  |  |  |  |  |  |  |  |  |  |

* George's group E (his measurements).

Table II.—$3\,{}^2D \rightarrow 1\,{}^2S$.

| $n', n''$. | Int. | $B_2$ (Q heads). | | Int. | *$B_1$ (R heads). | |
|---|---|---|---|---|---|---|
| | | λ. | $\nu_{\text{vac.}}$ | | λ. | $\nu_{\text{vac.}}$ |
| 0, 0 | 8 | 4950·767 | 20193·27 | | 4937·27 | 20248·47 |
| 1, 1 | 7 | 52·568 | 85·93 | | 38·75 | 42·40 |
| 2, 2 | 6 | 54·281 | 78·95 | | 40·08 | 36·96 |
| 3, 3 | 5 | 55·905 | 72·34 | | 41·34 | 31·79 |
| 4, 4 | — | — | (66·04) | | 42·53 | 26·92 |
| 5, 5 | 4 | 58·934 | 60·02 | | 43·61 | 22·50 |
| 6, 6 | 4 | 60·343 | 54·29 | | 44·63 | 18·33 |
| 7, 7 | 3 | 61·672 | 48·88 | | 45·56 | 14·53 |
| 8, 8 | 3 | 62·882 | 43·98 | | 46·35 | 11·30 |
| 9, 9 | 2 | 64·056 | 39·21 | | 47·25 | 07·63 |
| 10, 10 | 2 | 65·121 | 34·90 | | | |
| 11, 11 | — | — | (30·85) | | | |
| 12, 12 | 1 | 67·05 | 27·08 | | | |
| 13, 13 | 1 | 67·866 | 23·77 | | | |
| 14, 14 | 0 | 68·66 | 20·55 | | | |
| 15, 15 | 0 | 69·42 | 17·44 | | | |

* George's data, corrected to be uniform with the author's measurements.

It may be noted that, using the conditions established in Paper I, we can show that in this system the (0, 0) and (0, 1) sequences will both run to tails at about the 39th and 52nd members respectively. The plates taken show that both sequences exhibit condensations in about the expected positions.

The above system is notably different from the $2\,{}^2S \rightarrow 1\,{}^2S$ systems of CaF and SrF, in that the (0, 0) and (0, 1) sequences appear. In the latter the (0, 0) and (1, 0) sequences are found. I am unable to suggest any reason why positive values of $\Delta n$ are preferred in one case, and negative values in the other.

Table II gives the data of $B_2$ and $B_1$ which are believed to be (0, 0) sequences of associated Q and R branches. This appears to constitute a complete and independent system, of which this one sequence $\Delta n = 0$ is the only representative. It is, therefore, not possible to evaluate the vibrational constants of the initial state directly, but this may be done indirectly by using equations (1) and (2). The $B_2$ sequence is given by:

$$\nu = 20193\cdot250 - 7\cdot4554n'' + 0\cdot15977n''^2 + 0\cdot000193n''^3.$$

Accepting the values of $a''$, $b''$, and $c''$ from equation (2) we thus find

$$\nu_e = 20193\cdot25 \quad a' = 457\cdot189 \quad b' = 1\cdot8720 \quad c' = + \left\{ \begin{array}{c} 0\cdot01665\ (0, 0) \\ \\ 0\cdot01370\ (0, 1) \end{array} \right\}. \qquad (3)$$

We have assumed in doing this that both systems have a common final state (which is the normal one), but this is justified by Walters and Barratt's absorption data. We have labelled this system $3\,{}^2D \rightarrow 1\,{}^2S$ on the basis of a comparison of the electronic energy levels found in the atom $Ba^+$ with those of the molecule BaF. It is to be expected (as Mulliken* has pointed out) that considerable similarity may be found between these, since the valence electron of the molecule is in effect associated with the barium ion, the other electron having passed to the fluorine atom to complete the stable " neon " configuration. The low-lying levels of the singly ionised barium atom are shown to scale in fig. 1. It is interesting to compare this with fig. 2 which exhibits the electronic levels of the barium fluoride molecule. Such a transition as ${}^2D \rightarrow {}^2S$ violates the selection principle of *atomic* spectra since $\Delta k = 2$, but it may be remarked that violations of the type $\Delta k = 0$ are common in *molecular* spectra. From the selection principle of inner quantum numbers, viz., $\Delta j = \pm 1, 0$, it follows that only one of the two conceivable electronic transitions will be allowed; that from ${}^2D$ ($k = 3$, $j = 1\frac{1}{2}$) to ${}^2S$ ($k = 1, j = \frac{1}{2}$). This is in agreement with the observation of one strong system only. The best test of the electronic character of the system would lie in fine structure analysis of these bands, but this is probably beyond the power of any grating at present in existence. If the interpretation given is correct, this system will furnish, as far as I am aware, the first recorded example of the D → S molecular transition.

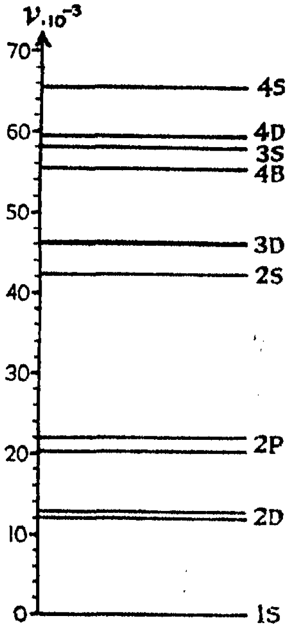

FIG. 1.—Energy Levels of the Atom $Ba^+$.

In Walters and Barratt's paper there are recorded in the absorption spectrum of BaF three very strong bands at λλ 7358, 7117 and 6911. These have no counterpart in recorded emission spectra, and it remains to determine in what relationship they stand to the systems already analysed. With this in view a spectrogram of the barium fluoride arc in air was taken on a small constant deviation type spectrograph, and a sequence was observed at the limit of the red region. The measured wave-lengths were approximately λλ 6912, 6934, 6959, and 6983. Insensitivity of the plate and the presence of continuous spectrum made it impossible to proceed further into the red. It is clear, however, that the leading member of this sequence is in all probability identifiable with the third of the above bands mentioned by Walters and Barratt.

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* 'Phys. Rev.,' vol. 26, p. 29 (1925).

In the paper by George, to which several references have been made,* there is given a list of bands attributed to barium oxide. Among these are four bands in remarkably close agreement with those mentioned. In view of this, the supposed " BaO " data were examined, and it was found possible to analyse the system completely. The results are given in Table III. Applying

Table III.—2 $^2$D → 1 $^2$S.

| Notes. | $n', n''$. | Q heads. | | R heads. | |
|---|---|---|---|---|---|
| | | λ. | $\nu_{vac.}$ | λ. | $\nu_{vac.}$ |
| *a, b* | 1, 0 | 6912·217 | 14463·16 | 6909·495 | 14468·85 |
| *a* | 2, 1 | 35·391 | 414·83 | 32·650 | 420·54 |
| *a* | 3, 2 | 58·771 | 366·40 | 56·4 | 371·29 |
| *a* | 4, 3 | 82·302 | 317·98 | 79·483 | 323·76 |
| *b* | 0, 0 | 7119·306 | 14042·45 | 7115·974 | 14049·02 |
| | 1, 1 | 42·038 | 13997·75 | 38·817 | 004·07 |
| *b* | 0, 1 | 7363·449 | 13576·85 | 7359·328 | 13584·46 |
| *c* | 1, 2 | 85·68 | 536·00 | 81·67 | 543·35 |
| | 2, 3 | 7408·29 | 494·68 | 7404·244 | 502·25 |
| | 3, 4 | 30·99 | 453·46 | 26·60 | 461·41 |

*a* Observed on my emission plates.
*b* Observed by Walters and Barratt in absorption.
*c* This value corrects an error in George's wave-length.

previous methods to these data I found for the vibrational constants of the initial and final electronic states :—

$$\nu_e = 14042\cdot02 \quad \left.\begin{array}{l} a' = 423\cdot133 \quad b' = 2\cdot1108 \quad c' = +0\cdot1166 \\ a'' = 466\cdot805 \quad b'' = 1\cdot6558 \quad c'' = + \left\{\begin{array}{l} 0\cdot0983 \ (1,0) \\ 0\cdot0216 \ (0,0) \end{array}\right. \end{array}\right\}. \qquad (4)$$

This exhibits remarkably close agreement of the final state, with that already derived from BaF in equation (2). Bearing in mind the peculiar discrepancy in $b''$ as determined from the various systems of CaF and SrF, a feature believed to be common to all the alkaline earth fluorides, we may definitely identify the final state of the above system of bands with that already determined for BaF. George's supposed barium oxide origin for the bands must therefore be abandoned. The three bands observed strongly in absorption are seen from Table III to be (0, 1), (0, 0) and (1, 0). At the relatively high temperatures (1000 to 1200° C.) used by Walters and Barratt, it is to be expected that a considerable proportion of molecules will be in one-quantum states, as absorption of the (0, 1) band requires. The new system is believed to arise from the electronic transition $2\,{}^2D \rightarrow 1\,{}^2S$, and it has been labelled as such in Table III and fig. 2. Reference to fig. 1 reveals a level $2\,{}^2D$ below $2\,{}^2P$ in the $Ba^+$ atom. In the $Mg^+$ atom this level has not been recorded, but in $Ca^+$, $Sr^+$, and $Ba^+$, it appears as the final level of a Bergmann (or fundamental) series. In view of the electron transition $3\,{}^2D \rightarrow 1\,{}^2S$ to which the band system recorded in Table II has been attributed, it seems reasonable to attribute this band system to $2\,{}^2D \rightarrow 1\,{}^2S$, for it is found in about the expected region and has the same structural characteristics.

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* See 'Données Numériques de Spectroscopie,' extrait du vol. 4, p. 135.

It is indeed remarkable that the system $2\,{}^2P \rightarrow 1\,{}^2S$, which has been so dominant in CaF and SrF, should be unrecorded in BaF, and that systems of the ${}^2D \rightarrow {}^2S$ type should appear. The system we have just considered (*vide* Table III) is in the region where we may expect to find such a ${}^2P \rightarrow {}^2S$ system. Reference to Tables V and IX of Paper I indicates the progressive lowering of analogous energy levels as the molecule becomes more massive, and we should expect the ${}^2P$ levels in the neighbourhood of 14000 to 15000 ν. On the assumption that the doublet interval $({}^2P_2 - {}^2P_1)$ is a function of the molecular number, I have used the data for MgF, CaF, and SrF, and found by a rough extrapolation that a doublet interval of the order of 600 ν may be anticipated for BaF. (Mecke has recorded for BaF, a doublet interval of 660 ν, but I have been unable to find any experimental evidence in support of this amongst available data. It is presumed to be a value calculated from theoretical considerations.) There is no evidence of any doublet interval of this order in the data of Table III, nor are there any absorption bands of Walters and Barratt in the extreme red unaccounted for. We are obliged therefore either to conclude that in the BaF molecule the $2\,{}^2P$ level lies below the $2\,{}^2D$ level, in which case the $2\,{}^2P \rightarrow 1\,{}^2S$ system will lie in the near infra-red, or, alternatively, that it is considerably weaker than its analogues in CaF and SrF, and has been unrecorded owing to the rapidly diminishing sensitivity of photographic plates in the red region.

Fig. 2 gives a picture of the energy levels of the BaF molecule. The full levels are electronic, and the broken lines are vibrational levels. The transitions indicated are of the leading member (only) of each sequence. In Table IV are summarised the constants of the BaF molecule.

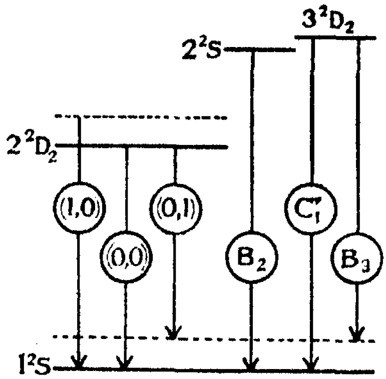

FIG. 2.—Energy Levels of the BaF Molecule.

Table IV.

| Level. | Energy. | | a ($\omega_0$). | b ($\omega_0 x$). | c. |
|---|---|---|---|---|---|
| | $\nu$. | Volts. | | | |
| $1\,{}^2S$ | 0 | — | *464·644 | 2·0318 | $\left\{\begin{array}{l}+0{\cdot}01645\\+0{\cdot}01351\end{array}\right.$ |
| $2\,{}^2D_2$ | 14042·02 | 1·733 | 423·133 | 2·1108 | +0·01166 |
| $2\,{}^2S$ | 19991·97 | 2·468 | 452·464 | 1·8767 | +0·01569 |
| $3\,{}^2D_2$ | 20193·25 | 2·493 | †457·189 | 1·8720 | $\left\{\begin{array}{l}+0{\cdot}01665\\+0{\cdot}01370\end{array}\right.$ |

* Values of equation (2) from the $2\,{}^2S \rightarrow 1\,{}^2S$ system. See also equation (4) for those from the $2\,{}^2D \rightarrow 1\,{}^2S$ system.

† Deduced by assuming the above constants for $1\,{}^2S$.

### *The Magnesium Fluoride Bands.*

This molecule (MgF) presents phenomena in great contrast to those of BaF. One system only has been recorded by Mecke, and this comprises the whole of the experimental emission data. This system, which is in the near ultra-violet, is undoubtedly due to the transition $2\,{}^2P \rightarrow 1\,{}^2S$. The measurements of Datta have been used for purposes of analysis. These are arranged in Table V together with the quantum numbers assigned to each band. $D_1$, $B_1$, and $E_1$ are the (1, 0), (0, 0), and (0, 1) sequences of Q branches arising from one of the doublet levels. $D_1'$, $B_1'$, and $E_1'$ are the associated sequences of P branches. There is little doubt that the (0, 0) band of $B_1$ has not been recorded by Datta. Its position at $\nu$ 27833·3 brings the P–Q interval for $B_1B_1'$ close to the value of $D_1D_1'$. It is apparent from their general disposition that $B_1''$ (Q heads) and $B_1'''$ (P heads) are the (0, 0) sequences, and

Table V.—(Datta's Measurements)—(2 $^2$P → 1 $^2$S).

| n′, n″. | B$_1$ (Q heads). |  | B$_1$′ (P heads). |  | B$_1$″ (Q heads). |  | B$_1$‴ (P heads). |  |
|---|---|---|---|---|---|---|---|---|
|  | λ. | $\nu_{vac.}$ | λ. | $\nu_{vac.}$ | λ. | $\nu_{vac.}$ | λ. | $\nu_{vac.}$ |
|  |  |  |  |  |  |  | *3599·26 | 27775·61 |
| 0, 0 | ‡(3591·82) | (27833·15) | 3592·80 | 27825·47 | 3594·22 | 27814·55 | 3595·69 | 27803·18 |
| 1, 1 | 88·19 | 861·28 | 89·11 | 854·15 | 90·58 | 842·74 |  |  |
| 2, 2 | 84·59 | 889·26 | 85·42 | 882·80 | 86·94 | 871·00 |  |  |
| 3, 3 | 80·98 | 917·36 | 81·80 | 911·13 | 83·30 | 899·30 |  |  |
| 4, 4 | 77·41 | 945·21 | 78·06 | 940·15 | 79·66 | 927·50 |  |  |
| 5, 5 | 73·79 | 973·51 | 74·48 | 969·12 | 76·09 | 955·53 |  |  |
| 6, 6 | 70·28 | 28001·15 | 71·98 | 993·95 | 72·65 | 983·07 |  |  |
| 7, 7 |  |  |  |  | 68·0 | 28011·20 |  |  |

| n′, n″. | E$_1$ (Q heads). |  | E$_1$′ (P heads). |  | (Q heads). |  | E$_1$″ (P heads). |  |
|---|---|---|---|---|---|---|---|---|
|  | λ. | $\nu_{vac.}$ | λ. | $\nu_{vac.}$ | λ. | $\nu_{vac.}$ | λ. | $\nu_{vac.}$ |
| 0, 1 | 3682·28 | 27149·43 | 3682·82 | 27145·44 |  |  | 3685·79 | 27123·57 |
| 1, 2 | 77·36 | 185·73 | 77·92 | 181·69 |  |  | 80·80 | 160·14 |
| 2, 3 | 72·50 | 221·70 | 73·06 | 217·60 |  |  | 75·91 | 196·44 |
| 3, 4 | 67·69 | 257·31 | 68·26 | 253·13 |  |  | 71·04 | 232·47 |
| 4, 5 | 62·96 | 292·58 | 63·52 | 288·32 |  |  | 66·23 | 268·23 |
| 5, 6 | 58·28 | 327·48 | 58·87 | 323·15 |  |  | 61·46 | 303·71 |
| 6, 7 | ‡53·57 | 362·70 | 54·25 | 357·61 |  |  | 56·73 | 338·99 |
| 7, 8 | ‡49·04 | 396·66 | 49·69 | 391·72 |  |  | 52·07 | 373·86 |
| 8, 9 |  |  | 45·19 | 425·50 |  |  | 47·46 | 408·52 |
| 9, 10 |  |  | 40·76 | 458·90 |  |  | 42·93 | 442·91 |
| 10, 11 |  |  | 36·42 | 491·71 |  |  | 38·41 | 477·03 |
| 11, 12 |  |  | 32·20 | 524·62 |  |  | 33·94 | 510·87 |

| n′, n″. | D$_1$ (Q heads). |  | D$_1$′ (P heads). |  |
|---|---|---|---|---|
|  | λ. | $\nu_{vac.}$ | λ. | $\nu_{vac.}$ |
| 1, 0 | 3502·44 | 28543·37 | 3503·36 | 28535·88 |
| 2, 1 | 3499·88 | 564·24 | 00·81 | 556·66 |
| 3, 2 | 97·35 | 584·90 | 3498·29 | 577·22 |
| 4, 3 | 94·84 | 605·35 | 95·80 | 597·57 |
| 5, 4 | 92·41 | 625·41 | 93·31 | 617·96 |
| 6, 5 | †90·08 | 644·43 | 90·88 | 637·95 |
| 7, 6 | 87·54 | 665·37 | 88·48 | 657·56 |
| 8, 7 | 85·17 | 684·78 | 86·11 | 677·04 |
| 9, 8 | 82·81 | 704·21 | 83·78 | 696·21 |
| 10, 9 | 80·50 | 723·25 | 81·48 | 715·25 |
| 11, 10 | ‡78·33 | 741·16 | 79·19 | 734·15 |
| 12, 11 | ‡76·32 | 757·86 | 76·96 | 752·56 |
| 13, 12 |  |  | 74·73 | 771·01 |
| 14, 13 |  |  | 72·55 | 789·08 |
| 15, 14 |  |  | 70·48 | 806·24 |
| 16, 15 |  |  | 68·46 | 823·01 |

| n′, n″. | Isotopic Q heads of D$_1$. |  |
|---|---|---|
|  | λ. | $\nu_{vac.}$ |
| 1, 0 | 3503·30 | 28536·38 |
| 2, 1 | 00·62 | 558·23 |
| 3, 2 | 3498·10 | 578·80 |
| 4, 3 | 95·56 | 599·56 |
| 5, 4 | 93·11 | 619·62 |
| 6, 5 | 90·61 | 640·12 |
| 7, 6 | 88·33 | 658·84 |
| 8, 7 | 86·0 | 678·0 |

( ) Value calculated, not observed.

† Value smoothed before computation.

* Spurious measurement.

‡ Value omitted in computation.

that $E_1''$ is the (0, 1) sequence associated with the other level of the doublet. The precise assignment of quantum numbers to these, however, raises one or two problems which may be mentioned at this stage. Taking the first *recorded* head in each of $B_1''$ and $B_1'''$, the P–Q interval suggests that the first member (0, 0) of $B_1''$ has not been recorded—precisely as occurred in connection with $B_1$ and $B_1'$. If, however, we deduce ν 27786·3 as the first member of $B_1''$ and adopt this as the (0, 0) band, the electronic doublet interval ($^2P_2 - {}^2P_1$) becomes 47 ν, as compared with 18·6 ν otherwise. If the doublet separation is plotted against molecular number for CaF and SrF, and if it is assumed that the one will approximately vanish with the other, it is apparent that the value 18·7 ν is much the more probable for MgF. It has, therefore, been decided to retain ν 27814·5 as (0, 0) band of $B_1''$, and to regard the first recorded member of $B_1'''$ as fictitious. This is quite possible owing to the extreme faintness of $B_1'''$, as a glance at Datta's plate will show. Accepting ν 27814·5 as the (0, 0) Q head, it is easy to calculate that the (0, 1) Q head should be located at ν 27132·4. This sequence clearly is not recorded, but at the expected interval of about 9 ν to the low frequency side we find the (0, 1) P-head sequence named $E_1''$. On no other assumption, except that of the spurious nature of the faint band at ν 27775·6, can the sequence $E_1''$ be satisfactorily explained. In fig. 3 are shown the transitions for the leading member of each sequence. The electronic doublet interval is given as 18·6 ν. Mecke gives 22 ν, but he has used the P heads in obtaining this. The former value obtained from the Q heads is the more accurate.

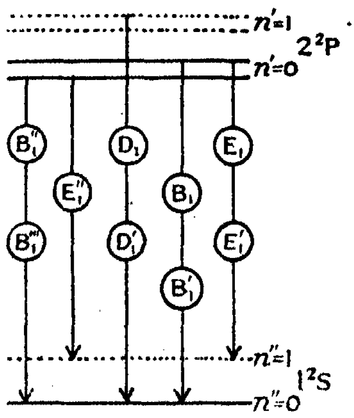

FIG. 3.—Energy Levels of the MgF Molecule.

Expressions have been obtained for the three sequences $D_1$, $B_1$, and $E_1$, viz. :—

$$(D_1)\quad \nu = 28543{\cdot}38 + 20{\cdot}963n'' - 0{\cdot}1083n''^2.$$

$$(B_1)\quad \nu = 27833{\cdot}15 + 28{\cdot}111n'' - 0{\cdot}0161n''^2,$$

$$(E_1)\quad \nu = 27112{\cdot}76 + 36{\cdot}837n'' - 0{\cdot}1750n''^2,$$

and from these by applying equation (1) to $D_1$ and $B_1$, and then to $B_1$ and $E_1$, we obtain two sets of vibrational constants which, however, are appreciably different. The constants of Table VI are approximately mean values of these and express the band system moderately well.

Table VI.

| Level. | Energy. | | $a$ ($\omega_0$). | $b$ ($\omega_0 x$). |
|---|---|---|---|---|
| | $\nu$. | Volts. | | |
| $1\,^2S$ | 0 | 0 | 686·80 | 3·95 |
| $2\,^2P_1$ | 27814·55 | 3·433 | 714·91 | 3·97 |
| $2\,^2P_2$ | 27833·15 | 3·436 | | |

The accuracy with which the system is represented does not justify a long extrapolation such as is necessary to determine the energy of dissociation of the molecule. It would appear, however, to be of the order of 33000 ν.

There remains one curious feature in connection with the magnesium fluoride spectrum to which attention should be drawn. With the exception of the faint heads of intensity (0) in BaF, the whole of the absorption bands of CaF, SrF and BaF are satisfactorily explained; in the case of MgF the situation is quite the reverse. In the table of the absorption bands of MgF* given by Walters and Barratt, the band at λ 3592 of intensity (2) is very probably a compound of the (0, 0) band heads of $B_1$, $B_1'$, $B_1''$, $B_1'''$, but I have been unable to account for any of the other bands. Some of these are very strong, and should be in the same neighbourhood as the familiar emission bands. Neither on Datta's plate, nor on special plates taken in the course of a search for these bands, have I found any evidence of them. There seem to be only two possible conclusions: either these bands represent a system or systems of MgF which are incapable of excitation in the electric arc, or they are absorption bands of some molecule other than MgF. I incline to the latter view. (Incidentally, it is believed that many of the faint absorption bands of intensity (0) in BaF are identifiable with these "MgF" absorption bands.)

### *The Vibrational Isotope Effect.*

A number of faint heads obviously associated with those of the $D_1$ sequence are recorded by Datta. These are isotopic heads arising from the molecule

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* Probably the direction of degradation of all these bands should be given as to the short wave side, and not as in the table. The band λ 3592 is certainly degraded to the short wave side. Incidentally, in the table of absorption bands of CaF, the first five bands should be marked as degraded to the *short* wave side.

$Mg^{25}F$. The main system is due to the more abundant species $Mg^{24}F$. The theoretical value of the isotopic coefficient for these molecules is given by $(\rho - 1) = - 0\cdot0088$. The experimental value has been calculated from the given data, and the mean value of $(\rho - 1)$ was found to be $- 0\cdot00774$. This measure of agreement is satisfactory for the given data. The mean separation of the isotopic heads is only about 0·2 A.U. and the accuracy of measurement is probably not greater than 0·02 or 0·03 A.U.

In conclusion I should like to thank again Prof. J. J. Nolan of University College, Dublin, for the loan of the Rowland grating to me. I am indebted for assistance, on several occasions, with the experimental work to Mr. R. K. Asundi. Finally, I should like to acknowledge gratefully the use of a calculating machine, made possible by the Government Grant Committee of the Royal Society.

### *Summary.*

(1) A quantum analysis has been made of the gross structure of the band spectra of the BaF and MgF molecules. For the former molecule new measurements have been made in the first order of a 21-foot Rowland grating.

(2) The familiar BaF bands in the green region are believed to constitute two systems, attributed to electron transitions $2\,{}^2S \rightarrow 1\,{}^2S$ and $3\,{}^2D \rightarrow 1\,{}^2S$.

(3) A number of bands measured by George, and attributed by him to BaO, have been analysed, and found to have their final state in common with the above BaF systems, thus proving their fluoride origin. The system is believed to be $2\,{}^2D \rightarrow 1\,{}^2S$.

(4) The suggested transitions of the type ${}^2D \rightarrow {}^2S$ are discussed, and are believed to be new to band spectra. The absence of the $2\,{}^2P \rightarrow 1\,{}^2S$ transition in BaF is remarkable.

(5) The recorded emission bands of MgF constitute a $2\,{}^2P \rightarrow 1\,{}^2S$ system, in which $\Delta 2\,{}^2P = 18\cdot6\ \nu$. The vibrational constants for these two states of the molecule are given.

(6) Definite evidence of the vibrational isotope effect occurs in the $D_1$ sequence of MgF. The observed value of the isotopic coefficient agrees within the limits of error with that calculated on the basis of two isotopes of magnesium of masses 24 and 25.

# *The Band Spectra associated with Zinc, Cadmium, and Mercury.*

By J. M. Walter, B.Sc., and S. Barratt, B.A., University College, London.

(Communicated by T. R. Merton, F.R.S.—Received September 7, 1928.)

The band spectra of the alkali metals are now well known, and it has been established that they are due to a small proportion of diatomic molecules, which are normally present in the vapours of these metals. It is as yet uncertain how many other metals, with vapours which, according to the ordinary methods of measurement, appear to be monatomic, give similar spectroscopic proof of association. Throughout a large number of experiments with the saturated vapours of the alkaline earth elements, up to 1200° C., we have found no evidence of band spectra which can be attributed to diatomic molecules of these metals. The elements of Group II*b* of the Periodic Table are much more interesting in this respect, and it is with experiments on the absorption spectra of these that this communication is concerned.

There have been several recent investigations of the vapours of zinc, cadmium, and mercury, and quite extensive band systems have been ascribed to them. It appeared to us, however, that the origin of some of the bands had not been completely established, and, in fact, we have now found that many of them are due to impurities of various kinds which may contaminate commercial samples of these metals; but even rejecting these impurity spectra, there remains evidence for association of the atoms in the vapours of all three elements.

It is often difficult, owing to the extreme sensitivity of spectroscopic methods, to assign a band spectrum to a particular molecule with certainty. For example, the most prominent features in the absorption spectrum of the vapour of commercial calcium are the bands of calcium subchloride and of sodium; though neither chlorine nor sodium can be present in more than very small amounts. The "cadmium" and "zinc" bands, and some of the "mercury" bands that have been listed, have a somewhat analogous origin, though the molecules responsible for them are not so easily identified, as none of the bands have been previously described, and as some of the impurities are rather unsuspected ones. It is only safe to assume that a given band system is due to a metal molecule such as $Cd_2$, when it has been shown that it can be observed with equal ease in samples of the metal from independent sources, and when its intensity is neither sensibly increased, nor decreased, by the introduction of traces of other elements.

In the present experiments, we first proved the non-metallic origin of most of the spectra by observing their total disappearance when a trace of sodium or potassium vapour was introduced into the absorbing column. This indicated that the molecules responsible for the bands thus repressed, contained electronegative elements which could be removed as the sodium or potassium salts. The probable electronegative impurities in these metals are limited, and the active ones were identified by increasing the quantity of each in turn, until every one of the band spectra had been obtained in an enhanced condition.

Many of the experiments were carried out in a form of apparatus already described,* consisting in essentials of an iron tube electrically heated, and provided with water-cooled quartz windows. The absorbing column was about 9 inches long. Such an apparatus has the advantage of rapidity in working, but all the conclusions were confirmed later, by experiments in which the vapours were enclosed in sealed quartz tubes with plane end windows. The metal was placed in a side tube heated to a temperature below that of the main apparatus, and the temperature of this side tube therefore determined the concentration of vapour in the absorbing column. It is much easier to exclude impurities from this form of apparatus than it is from the iron tube, so that it is more suitable for critical experiments on the origin of these spectra. The three metals will be treated separately in the succeeding sections.

## *Cadmium.*

Mohler and Moore in a recent paper,† have attributed seven band groups to this metal. We have come to the conclusion, however, that none of these bands, with the exception of Group I (see table below), can be due to a cadmium molecule. The remainder are due to impurities. We observed all the bands in a well developed state when cadmium was heated in an atmosphere of commercial (oxygen-containing) argon. All, except Group I, were weakened when hydrogen replaced the argon. Our next experiment was carried out in the presence of argon freed from oxygen by phosphorus, a trace of potassium metal having been added to the cadmium in order to combine preferentially with any electronegative impurities. The photograph showed none of the band systems except I, though the cadmium atomic lines were broader (and the density of the metal vapour greater) than in the previous experiments.

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* Walter and Barratt, 'Roy. Soc. Proc.,' A, vol. 119, p. 257 (1928).

† 'J. Opt. Soc. Amer.,' vol. 15, p. 74 (1927).

We then proceeded to find the impurities which must be added to cadmium to intensify each of the remaining systems.

Group II of Mohler and Moore was observed much enhanced in intensity when cadmium, with the addition of a little cadmium oxide, was heated in a quartz tube. A similar tube containing cadmium freed from superficial oxide showed only a trace of the same bands even at higher temperatures. We therefore attribute this spectrum to a compound containing both cadmium and oxygen, which must be appreciably volatile at these temperatures (500° to 800° C.).

Groups III, IV and V we have found, by a similar series of experiments, to be due to a cadmium chloride molecule. The spectrum is much more strongly developed, of course, with chloride added artificially to the metal, and we have recorded a few additional members of the band series.

Groups VI and VII eluded explanation for a considerable time. We attempted to intensify them, but without success, by adding to the vapour all the electronegative elements which were likely—and some which were unlikely—impurities. The clue to their origin came from a series of experiments in which a new sample of cadmium was used ; a sample from which we could not obtain the bands under any conditions. We next examined the spark spectra of the two specimens of metal, and found that our original material contained thallium, while the new specimen was free from it. It was then a simple matter to show that the bands in question are due to thallium chloride. They are very finely developed when thallous chloride is heated alone in either form of apparatus described above. We have not measured this spectrum completely as yet, but only sufficiently for identification. It should be mentioned that Mohler and Moore suspected that these bands might be due to an impurity present in their tubes.

Finally, to confirm the validity of this method of identifying the origin of the bands, we experimented with additions of traces of cadmium bromide and of cadmium iodide to the metal vapour, and as we expected, new band series appeared in absorption, evidently due to a volatile bromide and iodide of cadmium. These are briefly listed below. In a later communication we hope to describe them more fully, and to discuss the type of molecule responsible for them. It is probable that the molecules are of the subhalide type, *e.g.*, CdCl, both on theoretical grounds, and by analogy with the origin of the alkaline earth halide bands,* but we have not attempted to prove this point.

The band spectrum of cadmium in the glass and quartz regions would, therefore, seem to be limited to the structureless band at λ 2212. Of the origin of this there is, however, very little doubt. In the table below we have given first Mohler and Moore's tabulation, and in the other columns our own measurements on the component spectra.

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* Walter and Barratt, 'Roy. Soc. Proc.,' A, vol. 118, p. 120 (1928).

*Cadmium Bands.*

| Mohler and Moore. | | | $Cd_2$. | Cd + O. | Cd + Cl. | Tl + Cl. | Int. |
|---|---|---|---|---|---|---|---|
| Band Group. | λ. | Int. | λ. | λ. | λ. | λ. | |
| I | 2212 | | 2212 | | | | |
| | | | | 2856* | | | 00 |
| | | | | 2844* | | | 0 |
| | | | | 2825 | | | 00 |
| | | | | 2823 | | | 1 |
| | | | | 2810 | | | 3 |
| | | | | 2797 | | | 4 |
| | | | | 2783 | | | 1 |
| II | 2781 | | | 2781 | | | 3 |
| | | | | 2769 | | | 2 |
| | 2767 | | | 2767 | | | 4 |
| | 2756 | | | 2756 | | | 3 |
| | 2745 | | | 2745 | | | 5 |
| | 2736 | | | 2732 | | | 5 |
| | 2726 | | | 2721† | | | 3 |
| | 2709 | | | 2710* | | | 2 |
| | 2701 | | | 2699* | | | 2 |
| | 2694 | | | 2690† | | | 1 |
| | 2687 | | | | | | |
| | 2680 | | | 2679* | | | 0 |
| | 2673 | | | 2673* | | | 0 |
| | 2666 | | | | | | |
| | 2659 | | | 2660* | | | 00 |
| | 2653 | | | 2652* | | | 00 |
| | | | | 2644* | | | 00 |
| V. | 3177 | 8 | | | 3181 | | 5 |
| | 3170 | 4 | | | 3174 | | 2 |
| | | | | | 3172 | | 5 |
| | 3161 | 2 | | | 3163 | | 3 |
| | 3150 | 1 | | | 3152 | | 1 |
| | 3141 | 0 | | | 3145* | | 0 |
| | | | | | 3134* | | 0 |
| | | | | | 3127* | | 0 |
| | | | | | 3120* | | 00 |
| | | | | | 3115* | | 00 |
| IV. | 3104 | 1 | | | 3104* | | 0 |
| | | | | | 3100* | | 0 |
| | 3096 | 1 | | | 3097* | | 0 |
| | 3089 | 1 | | | 3090* | | 0 |
| | 3083 | 0 | | | 3083* | | 0 |
| | | | | | 3077* | | 0 |

Bands marked with an asterisk are those which it is difficult to measure satisfactorily.
† Indicates that the band head is masked by an emission line.

## *Cadmium Bands*—(continued).

| Mohler and Moore. | | | Cd$_2$. | Cd + O. | Cd + Cl. | Tl + Cl. | Int. |
|---|---|---|---|---|---|---|---|
| Band Group. | λ. | Int. | λ. | λ. | λ. | λ. | |
| | | | | | 3074 | | 2 |
| III. | 3071 | 4 | | | 3072 | | 5 |
| | 3066 | 2 | | | 3066 | | 4 |
| | 3059 | 1 | | | 3060 | | 3 |
| | 3052 | 1 | | | 3054 | | 2 |
| | 3046 | 1 | | | 3047† | | 1 |
| | 3040 | 1 | | | 3042 | | 1 |
| | 3035 | 0 | | | 3036 | | 0 |
| | 3029 | 0 | | | 3030 | | 0 |
| | 3023 | 0 | | | 3023 | | 0 |
| | | | | | 3018 | | 0 |
| | | | | | | 3323 | 0 |
| VII. | 3310 | 1 | | | | 3311 | 2 |
| | | | | | | 3309 | 0 |
| | 3300 | 1 | | | | 3300 | 3 |
| | | | | | | 3298 | 0 |
| | 3289 | 0 | | | | 3290 | 3 |
| | | | | | | 3288 | 0 |
| | | | | | | 3281 | 1 |
| | | | | | | 3279 | 0 |
| | | | | | | 3270 | 2 |
| | | | | | | 3268 | 0 |
| | | | | | (λ 3261 | in absorpt | ion). |
| VI. | 3249 | 4 | | | | 3251 | 4 |
| | | | | | | 3250 | 0 |
| | 3241 | 6 | | | | 3241 | 6 |
| | | | | | | 3240 | 2 |
| | 3232 | 8 | | | | 3232 | 8 |
| | | | | | | 3230 | 2 |
| | 3222 | 12 | | | | 3223 | 10 |
| | | | | | | 3221 | 2 |
| | | | | | | 3205 | 0 |
| | | | | | | 3193 | 1 |
| | | | | | | 3182 | 0 |

† Indicates that the band head is masked by an emission line.

## *Cadmium Bromide Bands.*

| $\lambda_{\text{air}}$. | $\nu_{\text{vac}}$. | Int. |
|---|---|---|
| 3551 | 28153 | 0 |
| 3538 | 28257 | 0 |
| 3525 | 28361 | 0 |
| 3510 | 28482 | 1 |
| 3499 | 28571 | 1 |
| 3486 | 28678 | 2 |
| 3475 | 28769 | 2 |
| 3464 | 28860 | 2 |
| 3452 | 28960 | 4 |
| 3430 | 29146 | 8 |
| 3418 | 29249 | 3 |
| 3407 | 29343 | 0 |

These bands are degraded to the long wave-length side.

*First Set of Cadmium Iodide Bands.*

| $\lambda_{air}$. | $\nu_{vac}$. | Int. |
|---|---|---|
| 4032 | 24795 | 0 |
| 4002 | 24980 | 0 |
| 3968 | 25195 | 1 |
| 3934 | 25412 | 2 |
| 3898 | 25647 | 2 |
| 3855 | 25933 | 3 |
| 3806 | 26267 | 6 |

These bands are diffuse so that the absorption maxima only have been approximately measured.

*Second Set of Cadmium Iodide Bands.*

| $\lambda_{air}$. | $\nu_{vac}$. | Int. |
|---|---|---|
| 4301 | 23244 | 0 |
| 4296 | 23271 | 1 |
| 4289 | 23309 | 2 |
| 4284 | 23336 | 3 |
| 4279 | 23363 | 10 |
| 4266 | 23435 | 6 |
| 4260 | 23468 | 4 |
| 4255 | 23495 | 2 |
| 4250 | 23523 | 0 |
| 4236 | 23601 | 1 |
| 4230 | 23634 | 3 |
| 4226 | 23656 | 2 |
| 4222 | 23679 | 0 |
| 4217 | 23707 | 00 |
| 4203 | 23786 | 0 |
| 4197 | 23820 | 1 |
| 4193 | 23843 | 0 |
| 4189 | 23865 | 00 |
| 4147 | 24107 | 2 |
| 4115 | 24295 | 1 |
| 4082 | 24491 | 1 |
| 4061 | 24617 | 0 |
| 4054 | 24660 | 00 |

The second set of cadmium iodide bands are degraded to the long wave-length side.

### *Zinc.*

Mohler and Moore observed three systems of bands in the absorption spectrum of zinc vapour (see table below). We have observed all three in the absorption of commercial zinc, but we have also found that two of them fail to satisfy our criteria for true metal spectra. These two systems vary in intensity from sample to sample, they are weakened by replacement of the argon by hydrogen, and they are entirely removed by the addition of a small quantity of an alkali metal. Group I is intensified, on the other hand, by introducing zinc oxide along with the zinc, into the furnace tube. It is not easy to obtain a satisfactory photograph of this spectrum, as with an excess of zinc oxide a continuous absorption obscures this wave-length region. Our measurements are, therefore, only approximate, and we are less satisfied with the observations on this spectrum than with those on any of the other bands.

Group II we have found to be the zinc chloride spectrum. As in dealing with the cadmium spectra, we thought it desirable to secure confirmatory evidence of our conclusions by obtaining analogous bands from the bromide. We found a new band system on the long wave-length side of the chloride spectrum, this has also been tabulated.

Group III is a true band spectrum of zinc, as it is consistently developed under all conditions in zinc vapour of sufficient density.

*Zinc Bands.*

| Mohler and Moore. | | | $Zn_2$. | Zn + Cl. | Zn + O. | Int. |
|---|---|---|---|---|---|---|
| Band Group. | λ. | Int. | λ. | λ. | λ. | |
| III. | 3050 | 1 | 3050 | | | 1 |
| II. | 2990 | 0 | | 2993 | | 0 |
| | 2976 | 1 | | 2976 | | 1 |
| | 2957 | 6 | | 2956 | | 8 |
| | 2943 | 3 | | 2943 | | 5 |
| | | | | 2941 | | 1 |
| | 2934 | 8 | | 2934 | | 10 |
| | | | | 2932 | | 1 |
| | 2923 | 2 | | 2923 | | 5 |
| | 2912 | 1 | | 2911 | | 2 |
| | 2902 | 0 | | 2903 | | 0 |
| | | | | | 2654 | 00 |
| I. | 2636 | | | | 2639 | 00 |
| | 2622 | | | | 2623 | 00 |
| | 2608 | | | | 2608 | 0 |
| | 2694 | | | | 2693 | 0 |
| | 2682 | | | | 2681 | 0 |
| | 2671 | | | | 2669 | 00 |
| | 2659 | | | | 2658 | 00 |
| | 2651 | | | | 2649 | 00 |
| | | | | | 2639 | 00 |

*The Zinc Bromide Bands.*

| $\lambda_{\text{air}}$. | $\nu_{\text{vac}}$. | Int. |
|---|---|---|
| 3113 | 32114 | 1 |
| 3110 | 32145 | 4 |
| 3102 | 32228 | 2 |
| 3093 | 32322 | 1 |
| 3085‡ | 32405 | 1 |
| 3071 | 32553 | 4 |
| 3068 | 32585 | 3 |
| 3064 | 32623 | 2 |
| 3060 | 32670 | 1 |
| 3056 | 32713 | 0 |
| 3052 | 32777 | 00 |
| 3048 | 32799 | 0 |
| 3044 | 32842 | 0 |
| 3039 | 32896 | 0 |
| 3035 | 32939 | 00 |
| 3031 | 32983 | 00 |
| 3027 | 33026 | 00 |

‡ This band was ill-defined, so that its centre only has been measured.
This band system is degraded to the long wave-length side.

## *Mercury.*

There can be no doubt that mercury vapour contains diatomic molecules. The corresponding band spectra are complex, and they have been carefully observed, both in absorption and emission. We have examined the behaviour of the known absorption bands by the methods already detailed, and we have found that they all have the characteristics of true metallic band spectra, with the exception of one system lying between λ 3000 and λ 2750. This band system has been recorded by Mohler and Moore, and by Moore in a subsequent paper.* It has also been more fully examined by Lord Rayleigh.† It appears in high pressure mercury vapour (above the normal boiling-point in our own apparatus), and the component bands are diffuse and difficult to measure. An excellent reproduction of this troublesome photographic subject is given in the third of the papers just quoted.

We have made many attempts to observe this spectrum in mercury vapour when it is heated in a carefully evacuated quartz tube, but always with negative results. It is interesting to note that Moore, in the later paper which appeared during the prosecution of our own experiments, concludes that this spectrum is probably not a true mercury spectrum, but, as he found that it was better developed in the presence of nitrogen, infers that a mercury nitride may be responsible for it. At one stage of the enquiry, we had come to the same opinion, but we ultimately found that the spectrum did not appear when oxygen was carefully excluded from the apparatus, however great a pressure of nitrogen was present. If a trace of mercuric oxide were introduced together with the mercury, the bands invariably appeared, irrespective of the presence of nitrogen. We can only conclude, as a result of our observations, that the bands are due to an association of mercury and oxygen, and not to the metal itself, or to a nitride.

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* 'Science,' vol. 66, p. 543, 1927.

† 'Roy. Soc. Proc.,' A, vol. 116, p. 702 (1927).

There is no conflict of experiment with the work of Lord Rayleigh, as his mercury column was in direct contact with air. In view of the discrepancy with the remaining investigations, we have spent much time in repeating our experiments. It may be taken as a slight confirmation of our conclusion that this band spectrum resembles Group II of cadmium, and Group I of zinc which, according to our experiments, are also oxide spectra.

*Mercury Bands.*

| | Mohler and Moore. | | Rayleigh. | Hg. | Hg + O. |
|---|---|---|---|---|---|
| **Band Group.** | λ. | Int. | λ. | λ. | λ. |
| I. | 2345 | 10 | 2341 to 46 | 2339 to 45 | |
| | 2339 | 5 | 2337 | 2336 | |
| | 2334 | 1 | 2333 | 2333 | |
| | | | 2330 | 2331 | |
| | | | 2741 | | 2739 |
| | | | 2747 | | 2747 |
| | | | 2755 | | 2753 |
| | | | 2762 | | 2760 |
| II. | 2772 | | 2768 | | 2767 |
| | 2778 | | 2776 | | 2774 |
| | 2786 | | 2784 | | 2784 |
| | 2794 | | 2791 | | 2794 |
| | 2801 | | 2799 | | 2800 |
| | 2810 | | 2807 | | 2808 |
| | 2818 | | 2815 | | 2814 |
| | 2826 | | 2825 | | 2824 |
| | 2835 | | 2833 | | 2834 |
| | 2846 | | 2843 | | 2843 |
| | 2857 | | 2853 | | 2854 |
| | 2866 | | 2864 | | 2864 |
| | 2876 | | 2874 | | 2875 |
| | 2886 | | 2884 | | 2885 |
| | 2889 | | 2895 | | 2807 |
| | 2909 | | 2907 | | 2907 |
| | 2921 | | 2918 | | 2918 |
| | 2932 | | 2930 | | 2931 |
| | | | 2943 | | 2043 |

All three systems are rather difficult to bring up satisfactorily in the vapours, and the molecules responsible for them are presumably only formed in small amounts. We found that if too much oxide were added to the metals all three systems became obscured by a continuous absorption, and were then quite impossible to photograph. The approximate measurements on the mercury bands which are recorded below were made on the intensity maxima, or centres, of the bands. We have also succeeded in finding chloride and bromide absorption bands of mercury in much the same spectral region. We have not included them in the table (see p. 209), as we are reserving them for a more detailed examination.

### *Summary.*

(1) The majority of the supposed band absorption spectra of zinc and cadmium, and one band system previously attributed to mercury, would appear to be oxide and chloride spectra.

(2) In the present experiments, the only bands found which can be attributed to zinc and cadmium themselves, are two weak and diffuse bands, one for each metal. The absorption spectrum of mercury, however, is much richer, and there is no doubt that mercury vapour contains diatomic molecules.

(3) The bromides of the three metals, together with the iodide of cadmium, all yield absorption band systems analogous to the chloride bands.

# *Observations in Connection with the Band Systems of the Fluorides of Beryllium and Magnesium*

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(Communicated by Prof. H. C. Plummer, F.R.S.—Received September 19, 1928.)

[PLATE 8.]

## 1. *Introductory.*

Until quite recently only two band-systems had been attributed to compounds of beryllium, BeF being the emitter of one system, which occurs in the ultra-violet, and BeO that of the other system, which lies in the visible region.* The former molecule is one of a series of thirteen-electron emitters of known band-systems, namely, CN, $N_2^+$, $CO^+$, BO, BeF, and MgH. The other molecule BeO is of interest on account of the fact that, like the emitter NaH,† it has the same number of electrons (twelve) as $C_2$, in which an electronic transition $^3P \rightarrow {}^3P$ is responsible for the emission of the Swan band-system.‡

The observations recorded in the first part of the present paper were made in order to ascertain whether any further bands might be attributed to BeF and BeO. The description of the newly observed bands (in section 4) is, for convenience, preceded by a discussion of the known systems. In the course of this discussion the data for BeF band-heads are re-examined and a modified interpretation of the heads is suggested (in section 2); and some corrections of, and additions to, the band-head data for the BeO system are also made (in section 3).

The molecule MgF which forms the subject of the latter part of the paper is one of four 21-electron emitters of known band-systems, namely, SiN, AlO,

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* Very recently two hydride systems have been discovered. One of them occurs in the visible region near λ 5000 and was recorded independently by W. W. Watson and by M. Peterson ('Phys. Rev.,' vol. 31, p. 1130 (1928), abstracts 85 and 86 respectively); it is attributed to an electronic transition $^2P \rightarrow {}^2S$ in the BeH molecule. The other system, which was recorded only by Watson (*loc. cit.*), extends from λ 3700 into the ultra-violet and consists of bands degraded to the red with single P and R branches only; Watson attributes it to an electronic transition $^1S \rightarrow {}^1S$ in the ionised molecule $BeH^+$.

† E. H. Johnson, 'Phys. Rev.,' vol. 29, p. 85 (1927). Mr. R. W. B. Pearse has kindly informed the writer that a further 12-electron emitter is possibly $MgH^+$, as the extensive ultra-violet system of magnesium hydride appears on analysis to be entirely analogous to Watson's $^1S \rightarrow {}^1S$ system of $BeH^+$ (see above footnote).

‡ Mulliken, 'Phys. Rev.,' vol. 29, p. 637 (1927); Pretty, 'Phys. Soc. Proc.,' vol. 40, p. 71 (1928).

MgF, and CaH—analogous to four of the above 13-electron emitters. Up to the present MgF has been represented by one ultra-violet band-system (section 5). A hitherto unrecorded band-system of MgF is now described (in section 6).

### 2. *The Doublet Band-system of* BeF.

The BeF system, which consists of bands degraded towards the red, was first described by S. Datta,* who obtained data for a very large number of band-heads in the second order of the 10-foot grating at the Imperial College, South Kensington (dispersion about 2·75 A./mm.). In every band Datta designated one head as $E_s$; for many of the bands he measured a second head of slightly greater wave-length, designated $E_s'$; and for some bands he gave a third head of considerably greater wave-length $E_s''$. The subscript $s$ had the values 1 to 6 for the different sequences (Datta's "Series") in the direction of increasing wave-lengths. Datta also obtained data for lines of the (0, 0) band at λ 3009 with still higher dispersion (third order of the grating), but they do not fully reveal the true band structure.

R. S. Mulliken† has assigned values of the initial and final vibrational quantum numbers, $n'$, $n''$, to the bands and has interpreted the first two heads $E_s$ and $E_s'$ respectively as the R and Q heads of one component band of a doublet, and the third (weaker) head $E_s''$ as one of the heads (probably the Q) of the other component band, the remaining (R) head possibly having escaped detection among the numerous band-lines. The $n'n''$ arrangement of Datta's wave-numbers for the band-heads is shown in Table I.‡ In addition to the bands of the BeF system shown in Table I, Datta recorded seven heads which do not form a sequence (Datta's group $E_6$, "not arranged in series"); further reference to these will be made in section 4. For the pairs of Q heads (*i.e.*, the second and third heads) Mulliken gave the approximate formula :§

$$\left.\begin{array}{l}\nu_{Q_2} = 33263\cdot5\\ \nu_{Q_1} = 33228\cdot5\end{array}\right\} + 1165\,(n'+\tfrac{1}{2}) - 8\,(n'+\tfrac{1}{2})^2 - 1262\,(n''+\tfrac{1}{2}) + 12\,(n''+\tfrac{1}{2})^2.$$

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[*] 'Roy. Soc. Proc.,' A, vol. 101, p. 187 (1922).

[†] 'Phys. Rev.,' vol. 26, p. 571 (1925).

[‡] The wave-numbers in all the tables of this paper are obtained from the observed wave-lengths with the aid of Kayser's "Tabelle der Schwingungszahlen."

[§] For every equation in this paper the form given in the text is that indicated by the new quantum mechanics, and the form according to the older quantum theory is added in footnotes. The original form of this equation is :—

$$\left.\begin{array}{l}\nu_{Q_2} = 33215\\ \nu_{Q_1} = 33180\end{array}\right\} + 1157n' - 8n'^2 - 1250n'' + 12n''^2.$$

Mulliken pointed out that the formulation of the R heads requires a large term in $n'n''$, about $-5\,(n'+\frac{1}{2})\,(n''+\frac{1}{2})$, due to the variation with $n'$ and $n''$ of the interval between band-origin and head, and that the variations of the mutual separations of the three observed heads may be ascribed to this fact together with the existence of appreciable differences in the values of B for the different heads.

It appears to the writer that this is not the most probable interpretation of the three heads observed by Datta. Table II shows the $n'n''$ arrangement of the mutual separations of the heads. It will be seen that the interval between the first and third heads increases rapidly from band to band with diminishing $n'$ in an $n'$ progression and with increasing $n''$ in an $n''$ progression, and that the interval between the second and third heads varies in a similar manner. This is known to be precisely the way in which the interval between the R and Q heads varies from band to band.* It is seen also in Table II that the interval between the first two heads varies in a different manner, and much more slowly, as compared with either of the two separations from the third head. From these facts it would appear that the first and second heads are both of the R type and the third of the Q type; that is to say, we have (in the order of diminishing wave-number) in each band $R_2$, $R_1$ and Q heads (with the other Q head missing) rather than $R_2$, $Q_2$ and $Q_1$ (with the other R head missing) as originally suggested by Mulliken. It is impossible to decide definitely from the existing data to which of the two R heads the observed Q head should be coupled, but it is probably $R_2$, *i.e.*, $Q_2$ is observed and $Q_1$ missing.

Alternatively the argument for the present, as against the former, interpretation may be stated with the help of the formulæ which have been derived to represent approximately the three heads, namely :†

$$\begin{aligned}\nu_{R_2} &= 33264\cdot3 + 1161\cdot6\,(n'+\tfrac{1}{2}) - 5\cdot88\,(n'+\tfrac{1}{2})^2 - 1255\cdot8\,(n''+\tfrac{1}{2}) \\ &\qquad + 11\cdot21\,(n''+\tfrac{1}{2})^2 - 4\cdot92\,(n'+\tfrac{1}{2})\,(n''+\tfrac{1}{2})\,; \\ \nu_{R_1} &= 33261\cdot5 + 1161\cdot2\,(n'+\tfrac{1}{2}) - 5\cdot67\,(n'+\tfrac{1}{2})^2 - 1255\cdot9\,(n''+\tfrac{1}{2}) \\ &\qquad + 11\cdot50\,(n''+\tfrac{1}{2})^2 - 5\cdot36\,(n'+\tfrac{1}{2})\,(n''+\tfrac{1}{2})\,; \\ \nu_{Q_2} &= 33226\cdot3 + 1172\cdot6\,(n'+\tfrac{1}{2}) - 8\cdot78\,(n'+\tfrac{1}{2})^2 - 1265\cdot6\,(n''+\tfrac{1}{2}) \\ &\qquad + 9\cdot12\,(n''+\tfrac{1}{2})^2.\end{aligned}$$

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* See Jevons, 'Roy. Soc. Proc.,' A, vol. 117, p. 361 (1928), for a general proof and for an illustration in the case of CS.

† The forms of these equations according to the older quantum mechanics are :—

$$\begin{aligned}\nu_{R_2} &= 33217\cdot3 + 1153\cdot3n' - 5\cdot88n'^2 - 1247\cdot1n'' + 11\cdot21n''^2 - 4\cdot92n'n''\,; \\ \nu_{R_1} &= 33214\cdot3 + 1153\cdot9n' - 5\cdot67n'^2 - 1247\cdot1n'' + 11\cdot50n''^2 - 5\cdot36n'n''\,; \\ \nu_{Q_2} &= 33179\cdot9 + 1163\cdot8n' - 8\cdot78n'^2 - 1256\cdot5n'' + 9\cdot12n''^2.\end{aligned}$$

## Table I.—Wave-numbers of Band-heads of Doublet System of BeF arranged in $n'$ and $n''$ Progressions and Sequences.

| $n'$ \ $n''$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 33217·6<br>214·6<br>180·0 | 31979·9<br>976·9<br>931·6 | 30767·6<br>766·1<br>— | | | | | | | | | | | | | | |
| 1 | 34366·7<br>362·3<br>333·0 | 33125·2<br>121·2<br>—(iv) | 31904·6<br>901·7<br>858·2 | 30710·7<br>708·9<br>— | | | | | | | | | | | | | |
| 2 | 35501·6<br>496·8<br>472·5 | 34255·5<br>251·3<br>225·0 | 33033·0<br>027·9<br>— | 31830·1<br>827·3<br>765·4 | 30654·0<br>651·9<br>— | | | | | | | | | | | | |
| 3 | | 35372·8<br>368·7<br>345·2 | 34145·7<br>142·0<br>118·2 | 32940·7<br>934·9<br>— | 31756·1<br>752·8<br>712·7 | 30597·5<br>595·6<br>— | | | | | | | | | | | |
| 4 | | | 35246·8<br>242·0<br>218·2 | 34037·6<br>035·2<br>013·2 | | 31682·9<br>679·5<br>639·4 | 30541·8<br>539·9<br>— | | | | | | | | | | |
| 5 | | | | 35119·9<br>117·1<br>092·4 | 33930 6<br>—<br>— | | 31610·6(ii)<br>606·6<br>569·6 | 30485·8<br>484·3<br>— | | | | | | | | | |
| 6 | | | | | 34995·8<br>993·2<br>966·8 | 33823·2<br>—<br>— | | 31538 2<br>534·5<br>498·0 | 30430·1<br>428·7<br>— | | | | | | | | |
| 7 | | | | | | 34873·6<br>871·0<br>840·8 | | | 31467·3<br>462·6<br>427·0 | 30373·9<br>—<br>— | | | | | | | |
| 8 | | | | | | | 34752·1<br>749·9<br>718·3 | | | 31396·5<br>—<br>— | 30318·4<br>318·0<br>— | | | | | | |
| 9 | | | | | | | | 34632 8<br>—<br>— | | | 31826·4<br>—<br>— | 30263·4<br>262·2<br>— | | | | | |
| 10 | | | | | | | | | 34510·7(i) | | | 31257·2<br>—<br>— | 30209·7(iii)<br>208·3<br>— | | | | |
| 11 | | | | | | | | | | | | | | 30153·8<br>152·4<br>— | | | |
| 12 | | | | | | | | | | | | | | | 30096·9<br>—<br>— | | |
| 13 | | | | | | | | | | | | | | | | 30041·7<br>—<br>— | |
| 14 | | | | | | | | | | | | | | | | | 29986·0<br>—<br>— |

*Notes to Table I.*

The first (top) wave-number for a given band pertains to the $B_2$ head, the middle one to the writer's $B_1$ (Mulliken's $Q_2$), and the third to the writer's $Q_2$ (Mulliken's $Q_1$).

For Datta's $\lambda_{air}$ and $\nu_{vac}$ data his 1922 paper (*loc. cit.*) should be consulted. The $\nu_{vac}$ values here tabulated are as given by Kayser's "Tabelle der Schwingungszahlen." Apart from the slight differences between these tables and those used by Datta for the reduction of $\nu_{vac}$ from $\lambda_{air}$ there is in several cases a discrepancy between Datta's $\lambda$ and $\nu$ values for one and the same head; the discrepancy has apparently arisen from an error (in MS. or in print) in one of the digits of either the $\lambda$ or the $\nu$ value. Which of the two is probably in error in a given case can pretty well be judged by considering the trend of the residuals given by the formulæ on p. 213. Whenever it was thought that Datta's $\lambda$ was listed as he intended the corrected $\nu$ has been entered here without comment.

In the following cases there is apparently an error in Datta's published $\lambda$:—

(i) $\nu$ 34510·7 is probably correct, and $\lambda$ should be 2896·80 instead of 2896·90.

(ii) $\nu$ 31610·6 is probably correct, and $\lambda$ should be 3162·58 instead of 3162·38.

(iii) Datta gives $\lambda$ 3308·25, $\nu$ 30208·78. The alternatives appear to be $\lambda$ 3308·25, $\nu$ 30218·8 : $\lambda$ 3309·25, $\nu$ 30209·7 and $\lambda$ 3309·35, $\nu$ 30208·8. The middle one of these has been adopted here.

(iv) Datta gives a head at $\lambda$ 3020 34, $\nu$ 33099·82, which would not fit well into the $n'n''$ scheme. Neither in Datta's reproduction nor in the author's plates does it appear certain that a head occurs here; the $\nu$ is therefore omitted in this table.

### Table II.—Separations of the Heads in the BeF Bands.

(*a*) First and Third Heads ($\nu_{R_2} - \nu_{Q_2}$).

| $n'$ \ $n''$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 37·6 | 48·3 | | | | | | | |
| 1 | 33·7 | | 46·4 | | | | | | |
| 2 | 29·1 | 30·5 | | 44·7 | | | | | |
| 3 | | 27·6 | 27·5 | | 43·4 | | | | |
| 4 | | | 28·6 | 24·4 | | 43·5 | | | |
| 5 | | | | 27·5 | | | 41·0 | | |
| 6 | | | | | 29·0 | | | 40·2 | |
| 7 | | | | | | 32·8 | | | 40·3 |
| 8 | | | | | | | 33·8 | | |

(*b*) Second and Third Heads ($\nu_{R_1} - \nu_{Q_2}$).

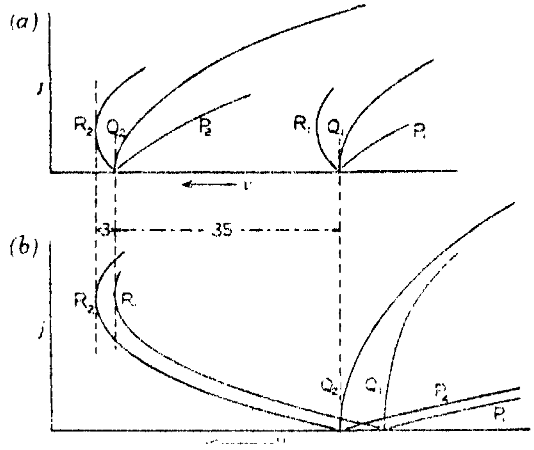
| $n'$ \ $n''$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 34·6 | 45·3 | | | | | | | |
| 1 | 29·3 | | 43·5 | | | | | | |
| 2 | 24·3 | 26·3 | | 41·9 | | | | | |
| 3 | | 23·5 | 23·8 | | 40·1 | | | | |
| 4 | | | 23·8 | 24·0 | | 40·1 | | | |
| 5 | | | | 24·7 | | | 40·0 | | |
| 6 | | | | | 26·4 | | | 36·5 | |
| 7 | | | | | | 30·2 | | | 35·6 |
| 8 | | | | | | | 31·6 | | |

(*c*) First and Second Heads ($\nu_{R_2} - \nu_{R_1}$).

| $n'$ \ $n''$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 3·0 | 3·0 | 1·5 | | | | | | | | | | | |
| 1 | 4·4 | 4·0 | 2·9 | 1·8 | | | | | | | | | | |
| 2 | 4·8 | 4·2 | 5·1 | 2·8 | 2·1 | | | | | | | | | |
| 3 | | 4·1 | 3·7 | 5·8 | 3·3 | 1·9 | | | | | | | | |
| 4 | | | 4·8 | 2·4 | | 3·4 | 1·9 | | | | | | | |
| 5 | | | | 2·8 | | | 4·0 | 1·5 | | | | | | |
| 6 | | | | | 2·6 | | | 3·7 | 1·4 | | | | | |
| 7 | | | | | | 2·6 | | | 4·7 | | | | | |
| 8 | | | | | | | 2·2 | | | | 0·4 | | | |
| 9 | | | | | | | | | | | | 1·2 | | |
| 10 | | | | | | | | | | | | | 0·5 | |
| 11 | | | | | | | | | | | | | | 1·4 |

The residuals ($\nu_{obs.} - \nu_{calc.}$) reach values rather greater than the limits of observational error, and indicate the necessity of cubic terms for more exact representation of the data. The term in $(n' + \frac{1}{2})(n'' + \frac{1}{2})$ to which Mulliken drew attention is found to be of the same high order for the second ($R_1$) heads as for the first ($R_2$), but is unnecessary in the case of the third ($Q_2$) heads.

Types of band-structure to be expected on the assumption of (*a*) Mulliken's and (*b*) the new interpretation are roughly indicated in the diagram; in the former the interval between the R head and origin of one component band is only about 3 cm.$^{-1}$, and the electronic doublet separation, $\Delta\nu_e = Q_2 - Q_1$, is of the order 35 cm.$^{-1}$, while in the present interpretation the interval between R head and origin is about 38 cm.$^{-1}$, and the electronic doublet separation $Q_2 - Q_1$ is of a much smaller order, since the interval between the $R_2$ and $R_1$ heads is about 3 cm.$^{-1}$.



A rough indication of types of band-structure to be expected on the assumption of (*a*) Mulliken's original interpretation of Datta's heads in the BeF bands, and (*b*) the revised interpretation now proposed. The three observed heads are indicated by the vertical broken lines, the missing head being $R_1$ in (*a*) and $Q_1$ in (*b*).

In a table of formulæ constants for the known band-systems of the 13-electron molecules BeF, BO, CN, $CO^+$, $N_2^+$, Mulliken (*loc. cit.*) showed Datta's system as the BeF analogue of the *less* refrangible systems of the other molecules (*i.e.*, the α system of BO, the red system of CN, the comet-tail system of $CO^+$ and an undiscovered near-infra-red system of $N_2^+$). The emission of these systems has been attributed by Mulliken* to an electronic transition $^2P \rightarrow {}^2S$ in the respective molecules. The BeF analogue of the *more* refrangible systems $^2S \rightarrow {}^2S$ of these emitters (*i.e.*, the β system of BO, the violet of CN, the first negative of $CO^+$ and of $N_2^+$) was shown in the same table as an undiscovered system in the further ultra-violet (below λ 2200 ?).

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* 'Phys. Rev.,' vol. 28, p. 1222 (1926).

The assignment of a transition $^2P \rightarrow {}^2S$ to the known BeF system still awaits confirmation by the rotational quantum analysis of the band-structure, which will, of course, also definitely settle the question as to whether the original or the revised interpretation of the heads is correct. Recently F. A. Jenkins* has undertaken the analysis with spectrograms taken under higher dispersion (second order of a 21-foot grating) than that employed by Datta, and has obtained some indication of a faint fourth head, *i.e.*, the missing $Q_1$, according to the new interpretation; the interval $Q_2 - Q_1$ in the (0, 0) band being about 4·8 cm.$^{-1}$.† If the transition is any other than $^2P \rightarrow {}^2S$ or $^2S \rightarrow {}^2P$ the observed small electronic interval of about 4·8 cm.$^{-1}$ is not itself an electronic doublet separation between two levels, but is the difference between two larger doublet separations. Further reference to this interval will be made later (end of section 5).

### 3. *The* $^1S \rightarrow {}^1S$ *Band-system of* BeO.

The BeO system, which was first described by W. N. Hartley‡ and measured later by Lecoq de Boisbaudran and A. de Gramont§ and by L. C. Glaser,‖ consists of four sequences of single-headed bands in the visible region degraded towards the red. A fifth sequence is added as a result of the present investigation. Glaser's data are shown in Table III together with the values of $n'$, $n''$ which were assigned by Mecke.¶ Glaser's wave-lengths for the (5, 4) and (6, 5) band-heads differ from Lecoq and de Gramont's by nearly 2 and 5·5 A.U. respectively.**

From the low dispersion spectrograms (from 14 to 12 A.U./mm. over the range λ 4500—λ 4200) taken in the course of the present work, it would appear that Lecoq and de Gramont's estimate is the nearer in each case. Neither of the heads is easy to locate with certainty, but fairly concordant results have been obtained from the less heavily exposed plates; in the more heavily exposed plates the real (5, 4) head is obscured by a mass of lines having a head-like edge in Glaser's position for this head, but no head is detectable in any plate in the position given by Glaser for the (6, 5) head.

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* The author has been informed of this work, which is still in progress, in letters from Dr. Jenkins and Prof. Mulliken.

† As roughly measured by the writer in a very beautiful print which Dr. Jenkins has kindly given to him.

‡ 'Phil. Trans.,' A, vol. 185, p. 161 (1894); 'Trans. Roy. Dublin Soc.,' vol. 7, p. 339 (1901); 'Roy. Soc. Proc.,' A, vol. 79, p. 242 (1907).

§ 'C. R.,' vol. 153, p. 318 (1911).

‖ Dissertation, Berlin, 1916; 'Ann. Physik,' vol. 68, p. 73 (1922).

¶ 'Phys. Z.,' vol. 26, p. 228 (1925).

** Kayser and Konen, 'Handbuch der Spectroscopie,' vol. 7, Pt. 1, p. 102 (1924).

Table III.—R Heads of $^1S \rightarrow {}^1S$ Band-system of BeO.

| $n'$ \ $n''$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|
| 0 | (4708·67)<br>21231·5 | (5054·10)<br>19780·4 | (5445·9)<br>18357·3 | | | | | |
| 1 | (4427·34)<br>22580·6 | (4732·66)<br>21123·9 | (5075·21)<br>19698·1 | (5462·7)<br>18300·9 | | | | |
| 2 | (4179·95)(ii)<br>23917·0 | (4451·79)<br>22456·6 | (4754·46)<br>21027·0 | (5094·64)<br>19623·0 | (5477·0)<br>18253·1 | | | |
| 3 | | (4204·21)(ii)<br>23779·0 | (4474·69)(i)<br>22341·7 | (4775·37)<br>20934·9 | (5111·97)<br>19556·5 | (5481·1)<br>18216·2 | | |
| 4 | | | [(4228·1)<br>23644·7] | (4496·47)<br>22233·4 | (4795·24)<br>20848·2 | (5127·25)<br>19498·2 | | |
| 5 | | | | [(4250·3)<br>23521·2] | (4517·3)(ii)<br>22130·9 | (4813·04)<br>20771·1 | (5140·53)<br>19447·8 | |
| 6 | | | | | | (4535·5)(ii)<br>22042·1 | (4827·35)<br>20709·5 | (5151·45)<br>19406·6 |

*Notes to Table III.*

(i) Glaser gives λ 4474·79 I.A.; but it should be 4474·69 if his ν be assumed correct.

(ii) Measured by the author; all the other data are Glaser's, checked by means of Kayser's "Tabelle der Schwingungszahlen."

[ ] Band-heads obscured by lines; positions estimated by means of formula (p. 219).

Four bands of the hitherto unrecorded sequence, $n'' - n' = -2$, have been recognised in the present spectrograms and are included in Table III. In the carbon arc fed with BeO, the (3, 1) band-head, which is probably the strongest of the new sequence, occurs between the λ 4216 (0, 1) and λ 4197 (1, 2) heads of the CN violet system. Under particularly favourable conditions (described in the following section) the CN bands are so much reduced relatively to the BeO system, that the (3, 1) head of the latter is easily detected and measured. The (2, 0) head remains hidden by the λ 4181 (2, 3) band of CN; it is just detectable, however, in the copper arc fed with BeO. The (4, 2) band is well developed in the best of the plates but its head cannot be located on account of its proximity to the Ca line λ 4226·72, which is overwhelmingly strong; the (5, 3) band is also present but its head is obscured by the Fe lines λλ 4250·134, 0·791.

The data for the six bands just discussed are :—

| Band, $(n', n'')$. | Glaser, $\lambda$ (I.A.). | Lecoq and de Gramont, $\lambda$ (I.A.). | Author. | |
|---|---|---|---|---|
| | | | $\lambda$ (I.A.). | $\nu_{\text{vac.}}$ |
| (5, 4) | 4515·25 | 4517·2 | 4517·3 | 22130·9 |
| (6, 5) | 4530·66 | 4536·1 | 4535·5 | 22042·1 |
| (2, 0) | | | 4179·95 | 23917·0 |
| (3, 1) | | | 4204·21 | 23779·0 |
| (4, 2) | | | [4228·1 | 23644·7] |
| (5, 3) | | | [4250·3 | 23521·2] |

The figures given in brackets for the (4, 2) and (5, 3) bands here and in Table III are estimated by means of a formula approximately representing the whole system* :—

$$\nu_{\text{head}} = 21287\cdot 0 + 1364\cdot 2\,(n' + \tfrac{1}{2}) - 5\cdot 90\,(n' + \tfrac{1}{2})^2 - 1479\cdot 1\,(n'' + \tfrac{1}{2})$$
$$+ 15\cdot 22\,(n'' + \tfrac{1}{2})^2 - 5\cdot 24\,(n' + \tfrac{1}{2})\,(n'' + \tfrac{1}{2}).$$

For the strong blue sequence $(n'' - n' = 0)$ Glaser measured the wavelengths of the band-lines in the second order of the 10-foot concave grating at the Imperial College, the dispersion being about 2·56 A./mm. Very recently Miss J. E. Rosenthal and F. A. Jenkins† have carried out the rotational quantum analysis of the bands of the three prominent sequences, $n'' - n' = +1$, 0 and $-1$, with plates of still higher dispersion (first and second orders of a 21-foot grating). They find that each band consists of a single P and a single R branch with only one missing line and no Q branch ; the system is due to an electronic transition ${}^1\text{S} \rightarrow {}^1\text{S}$, the final state being probably the normal state of the BeO molecule.

## 4. *New Bands of Beryllium Oxide or Fluoride.*

The spectra given by the flame surrounding the arc between carbon poles fed with several beryllium salts were examined under varying conditions by means of a Littrow quartz prism spectrograph giving dispersions of

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* Older quantum theory form :—

$$\nu_{\text{head}} = 21230\cdot 6 + 1356\cdot 7n' - 5\cdot 90n'^2 - 1466\cdot 5n'' + 15\cdot 22n''^2 - 5\cdot 24n'n''.$$

This formula, though not entirely satisfactory, leaves smaller and more widely distributed residuals $(\nu_{\text{obs.}} - \nu_{\text{calc.}})$ than that given by Mecke (*loc. cit.*), neglecting the large term in the $n'n''$, namely :—

$$\nu_{\text{head}} = 21231\cdot 6 + 1354n' - 8\cdot 0n'^2 - 1465n'' + 12\cdot 7n''^2.$$

† 'Phys. Rev.,' vol. 31, p. 705, abs. 2 (1928).

14·0 – 12·0 A.U./mm. at λ4500 – λ4200, and 5·9 – 4·0 A.U./mm. at λ3500 – λ3000.

With $BeF_2$ it was observed that, for a few minutes after freshly charging or recharging the positive pole with the salt, the arc was surrounded by a yellow flame, due, no doubt, to the abundance of sodium salts as impurities in the $BeF_2$ or the carbons or both. Subsequently, however, a bright blue flame appeared, the most favourable conditions being a relatively large current, say 10 to 12 amperes, and a large residue of the salt already added in several charges and used for the yellow-flame stage; the arc was comparatively quiet in the yellow-flame condition, but inclined to splutter in the blue-flame condition.

The yellow-flame showed the band-systems of both BeO and BeF, the latter being especially well developed. The outer part of the blue-flame, on the other hand, showed the visible BeO system very much more strongly developed (the blue colour is mainly accounted for by the 0 sequence of this system), the BeF system very much reduced in intensity, and the region between the CN λ 3590 sequence and the 0 sequence of the BeF system now occupied by an entirely different set of bands, which, like the BeF bands, are also degraded towards the red. Other Be salts tried ($BeCl_2$, BeO, $Be(NO_3)_2$) all gave results similar to those observed with $BeF_2$, the occurrence of the BeF system in the yellow-flame stage being probably accounted for by the presence of fluoride impurities in the salts and the carbons. BeO was found to be especially useful on account of the fact that although the BeF system given by the yellow-flame arc was never quite free from traces of the new bands, yet it was possible after a little experience to obtain the blue-flame stage under such conditions that it showed the BeO visible system and the new ultra-violet bands with hardly a trace of the BeF bands. The new bands were observed under the conditions described, both with carbons supplied commercially for ordinary use in projection lanterns and with Acheson graphite rods; and none of the bands was ever observed in the absence of the added Be salt.

Although the new bands extend over a region of more than 500 A.U., comparatively few well-marked heads occur. Table IV contains the data for the heads, and features which resemble heads, measured in several plates; the Fe lines occurring in the blue arc-flame itself were used as standards for the wave-lengths measurements in order to eliminate errors due to possible shifts. The spectrograms from which Plate 8 was made were obtained with BeO. Reproductions 1*a* and 2*a* are of the yellow-flame stage showing the 0, +1 and +2 sequences of BeF with a faint trace (in the original photograph) of the strongest of the new bands near λ 3371, while reproductions 1*b* and 2*b* are of the blue-flame stage, showing only the new bands (in the original negative it is just possible to detect the head of the BeF (0, 0) band at λ 3009·6). The λ 3590 sequence of CN bands and lines of Fe, Al, Be, Na and Cu occur as impurities in both conditions, (*a*) and (*b*).

Plate 8 shows that while the new bands do not form a number of regular sequences such as characterise the known band-systems of diatomic emitters, they occur in separate groups not wholly unlike those sequences. Three such groups occur respectively in the regions of the 0, +1, and +2 sequences of the BeF system; the second group is characterised by a well-marked (apparently triple) head near λ 3134, and the third has definite heads at λλ 3258·2 and 3269·1. On casual inspection it might appear that, while the (0, 1) band λ 3126·1 of BeF is absent in reproduction 2*b*, the neighbouring (1, 2) band λ 3133·7 is strongly developed but modified in intensity distribution. This, however, is not the case; not only does the head λ 3133·8 in reproduction 2*b* differ in wave-length by 0·1 A.U. from the BeF head, but the two differ markedly in appearance when examined under high magnification. Another new group with heads at and near λ 3504 runs into the CN λ 3590 sequence. The strongest group of the new bands has exceedingly well-marked heads at λλ 3371·1 and 3363·7, weaker but unmistakable heads at λλ 3359·4 and 3357·2, and probable but less certain heads at λλ 3378·3, 3361·9, etc. This group covers the region occupied by the seven bands of Datta's group $E_6$ which, as already mentioned (p. 212), were "not arranged in series," namely, λλ 3392·59, 3378·03, 3371·26, 3363·67, 3361·56, 3349·93, 3344·12. If allowance be made for the fact that Datta's measurements and the author's were made under entirely different conditions (*e.g.*, Datta's on plates showing the BeF system strongly, and the author's on plates with this system almost absent), the approximate coincidence of four wave-lengths in Datta's list with four in the present observations may perhaps be regarded as evidence for the identity of the groups. It appears, then, that the bands of Datta's group $E_6$ belong not to the BeF system, but to the "new" bands. Apart from this group, no bands listed by Datta occur in Table IV; only in two instances (λλ 3133·81 and 2930·05) does a wave-length given here approach as closely as 0·1 A.U. to one of Datta's.

Table IV.—Heads of New Bands of Beryllium Oxide or Fluoride. (Degraded towards the red.)

| Int. | $\lambda_{air}$. | $\nu_{vac}$. | Notes. | Int. | $\lambda_{air}$. | $\nu_{vac}$. | Notes. |
|---|---|---|---|---|---|---|---|
| 3 | 3514·69 | 28443·9 | *d* | 4 | 3269·09 | 30580·8 | *a* |
| 4 | 12·00 | 465·7 | *d* | 5 | 58·16 | 683·3 | *a* |
| 4 | 08·66 | 492·8 | *d* | 2 | 49·66 | 763·6 | *c* |
| 5 | 04·54 | 526·3 | *a* | | | | iii |
| 5 | 00·76 | 557·1 | *b* | 2 | 36·19 | 891·6 | *d* i |
| 4 | 3498·80 | 573·1 | *b* | 2 | 23·22 | 31015·9 | *b* |
| 4 | 95·10 | 603·3 | *b* i | 3 | 02·18 | 219·7 | *b* |
| 1 | 86·90 | 670·6 | *c* | 5 | 3145·62 | 781·1 | *b* |
| 3 | 64·30 | 857·6 | *c* | 5 | 34·90 | 889·7 | *b* |
| 3 | 39·23 | 29068·0 | *c* | 5 | 34·34 | 895·4 | *b* |
| 4*n* | 27·86 | 164·4 | *d* | 6 | 33·81 | 900·8 | *a* |
| 5*n* | 13·86 | 284·0 | *d* | 5 | 3077·97 | 32479·5 | *d* |
| 5 | 3378·34 | 591·9 | *c* ii | 4 | 52·4 | 752 | *d* iv |
| 4 | 76·47 | 608·3 | *d* | 4 | 38·97 | 896·3 | *d* |
| 8 | 71·11 | 655·3 | *a* ii | 2 | 28·97 | 33004·9 | *d* |
| 2 | 67·42 | 687·8 | *c* | 2 | 2975·35 | 611·0 | *d* |
| 2 | 64·46 | 713·9 | *c* | 0 | 68·26 | 680·0 | *d* |
| 8 | 63·73 | 720·4 | *a* ii | 1 | 65·88 | 707·0 | *d* |
| 2 | 61·86 | 736·9 | *b* ii | 0 | 51·39 | 872·5 | *d* |
| 4 | 59·39 | 758·8 | *a* | 2 | 30·05 | 34119·1 | *c* |
| 4 | 57·20 | 778·2 | *a* | 1 | 23·04 | 201·0 | *c* |
| 3 | 3280·95 | 30470·2 | *c* | 0 | 10·79 | 344·9 | *c* |

*Notes to Table IV.*

The character of the band-heads is indicated by the letters in italics :—*a*, certain ; *b*, fairly certain ; *c*, probable ; *d*, possible but somewhat doubtful.

i. Confused by a line.

ii. These four heads may be identical with four in Datta's group $E_4$, namely, λλ 3378·03, 3371·26, 3363·67, 3361·56.

iii. A probable band-head not listed is obscured by the strong Cu line λ 3247·55, ν 30783·6.

iv. There is certainly a band about here, but its head may not be located correctly.

The distribution of the new bands is far less regular than that of any bands which have been attributed to a diatomic molecule ; and it has not been possible to assign $n'$, $n''$ values. The observations do not settle the question of the emitting molecule ; it is evidently an oxide or a fluoride of beryllium, BeO or other oxide being suggested by the strong development of the bands under the same conditions as the $^1S \rightarrow {}^1S$ system of BeO, and $BeF_2$ being possible in view of the known presence of fluorides in the salts and the carbons used.

No bands attributable to BeCl and no further bands of BeF have been detected.

### 5. *The Doublet Band-system of* MgF.

The MgF band-system was discovered by C. M. Olmsted* and more completely observed by S. Datta† who recorded data (dispersion 2·75 A./mm.) for a large number of heads, to which $n'$, $n''$ values were subsequently assigned by R. Mecke.‡ The system lies in the region λ 3686—λ 3468, and consists of three sequences of bands degraded towards the further ultra-violet. As in the case of the BeF system, Datta observed three heads in many of the bands and either two or one in others. As far as the present writer is aware the significance of Datta's band-heads of MgF has never been adequately discussed; but Mecke has given the electronic doublet interval $\Delta\nu_e$ as 22 cm.$^{-1}$, and has represented one head of each band by the formula :—

$$\nu = 27810{\cdot}8 + 717{\cdot}3\,(n' + \tfrac{1}{2}) - 3{\cdot}80\,(n' + \tfrac{1}{2})^2 - 687{\cdot}8\,(n'' + \tfrac{1}{2}) + 3{\cdot}70\,(n'' + \tfrac{1}{2})^2.\text{§}$$

The heads in question, however, require for their more exact formulation a term in $n'n''$, which is neglected in this formula but is of the order $-1{\cdot}7\,(n' + \tfrac{1}{2})\,(n'' + \tfrac{1}{2})$; it is therefore evident that they are P-branch heads.

This doublet band-system of MgF appears to be analogous with those of BO (α system), CN (red system), and $CO^+$ (comet-tail system), each of which is due to an electronic transition $^2P \rightarrow {}^2S$. In the absence of a rotational quantum analysis of the MgF band-structure, which is very close and will require very high dispersion, this analogy affords the only evidence for the transition $^2P \rightarrow {}^2S$.

According to Birge's recent tables|| the visible doublet systems of the alkaline earth fluorides CaF, SrF, BaF are also due to $^2P \rightarrow {}^2S$ transitions. Mecke has included five systems, BeF, MgF, CaF, SrF and BaF, in a table¶ showing a steady decrease in each of the vibrational energy coefficients for the initial and final states as the number of electrons in the molecule increases; these coefficients for BeF are so little altered (apart from the use of the new mechanics form of the equations) in the present paper that it is needless to

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* 'Z. Wiss. Phot.,' vol. 4, p. 354 (1906).

† 'Roy. Soc. Proc.,' A, vol. 99, p. 436 (1921).

‡ Mecke, 'Z. Physik,' vol. 42, p. 412 (1927); also Mecke and Guillery, 'Phys. Z.,' vol. 28, p. 516 (1927).

§ The old quantum theory form is :—

$$\nu = 27825{\cdot}5 + 713{\cdot}5n - 3{\cdot}80n'^2 - 684{\cdot}1n'' + 3{\cdot}70n''^2.$$

|| 'Constants of Diatomic Molecules derived from Band Spectra Data,' International Critical Tables. The writer is indebted to Prof. Birge for the use of a MS. copy of these tables, including all band-systems analysed up to March, 1928.

¶ Mecke's Table 10, p. 412; Mecke and Guillery's Table X, p. 516.

repeat the table here. In another table* Mecke shows the steady increase of the origin separations $\Delta\nu_e$ with the number of electrons in the molecules MgF to BaF. Inserting the new value now proposed for BeF we have :—

| | BeF. | MgF. | CaF. | SrF. | BaF. |
|---|---|---|---|---|---|
| Number of electrons .......... | 13 | 21 | 29 | 45 | 65 |
| Approximate separation $\Delta\nu_e$ .. | 4·8 | 22 | 74 | 280 | 660 |

The significance of the regular increase exhibited is not apparent as, in the absence of analyses of the band-structures, it is not yet certain that all these systems are due to similar electronic transitions in the respective molecules.

### 6. *A New Band-system of* MgF.

The flame surrounding the arc between carbon poles fed with $MgF_2$ was examined with the Littrow quartz spectrograph, the current being about 10 amperes, as in the case of the corresponding observations (section 4) with $BeF_2$. The spectrum contained, in addition to the MgF band-system already described by Olmsted and by Datta, another, more refrangible, system of three sequences of bands degraded to the further ultra-violet from heads at λλ 2741·6, 2689·3, and 2636·4 respectively, the middle sequence being the strongest. No record of the latter system could be found in any publication accessible to the writer. Reproduction 3 in Plate 8 shows the new system, together with lines of Al, Pb and Fe, as developed in the above source : Mg lines are, of course, strongly developed, but none occur in the range reproduced.

The heads appear single under the dispersion used, which is from 3·22 to 2·81 A./mm. over the range λ 2740—λ 2630, *i.e.*, almost as big as that used by Datta for the BeF and MgF heads. The wave-lengths and wave-numbers obtained for the heads are arranged in $n'$ and $n''$ progressions and sequences in Table V. The data are closely represented by :—†

$$\nu_{\mathrm{P\ head}} = 37151\cdot7 + 757\cdot8\,(n'+\tfrac{1}{2}) - 6\cdot24\,(n'+\tfrac{1}{2})^2 - 715\cdot8\,(n''+\tfrac{1}{2}) + 3\cdot32\,(n''+\tfrac{1}{2})^2 + 1\cdot68\,(n'+\tfrac{1}{2})(n''+\tfrac{1}{2}).$$

The term in $n'n''$ is definitely necessary, as is expected for P-branch heads.

The distribution of the bands in a 0 sequence with weaker +1 and −1 sequences only is in theoretical accordance with the very small decrease in vibrational frequency indicated by this formula, and with the correspondingly

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* Mecke's Table 15, p. 418 ; also Mecke and Guillery, p. 485.

† Older quantum theory form :—

$$\nu_{\mathrm{P\ head}} = 37172\cdot4 + 752\cdot4\,n' - 6\cdot24\,n'^2 - 711\cdot6\,n'' + 3\cdot32\,n''^2 + 1\cdot68\,n'n''.$$

Table V.—P Heads of New Band-system of MgF. ($\lambda_{air}$ (I.A.) in italics.)

| $n'$ \ $n''$ | 0 | | 1 | | 2 | | 3 | | 4 | | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | *2689·35*<br>37172·7 | 708·8 | *2741·63*<br>36463·9 | | | | | | | | | | |
| | 745·8 | | 747·8 | | | | | | | | | | |
| 1 | *2636·45*<br>37918·5 | 706·8 | *2686·53*<br>37211·7 | 699·7 | *2738·02*<br>36512·0 | | | | | | | | |
| | | | 735·6 | | 737·3 | | | | | | | | |
| 2 | | | *2634·45*<br>37947·3 | 698·0 | *2683·82*<br>37249·3 | 692·0 | *2734·62c*<br>36557·3 | | | | | | |
| | | | | | 724·4 | | 726·4 | | | | | | |
| 3 | | | | | *2632·62c*<br>37973·7 | 690·0 | *2681·34*<br>37283·7 | 683·4 | *2731·41*<br>36600·3 | | | | |
| | | | | | | | 713·8 | | 715·0 | | | | |
| 4 | | | | | | | *2630·97c*<br>37997·5 | 682·2 | *2679·07c*<br>37315·3 | 674·6 | *2728·40*<br>36640·7 | | |
| | | | | | | | | | 703·1 | | | | |
| 5 | | | | | | | | | *2629·52*<br>38018·4 | | | *2725·60c*<br>36678·3 | |
| 6 | | | | | | | | | | | *?2628·30c*<br>38036·1 | | *2723·09*<br>36712·1 |

c Confused with Fe line in arc-flame.

small increase in moment of inertia which it accompanies. The emitter is clearly diatomic, and must be MgF or $MgF^+$, since the system could not be detected in plates taken with the other alkaline earth fluorides replacing the $MgF_2$ in the arc in air, or with MgO, $MgCl_2$ or metallic Mg.

Comparing the above formula with the approximate one quoted in section 5 (p. 223) for the previously known system of MgF, it will appear that, although the vibrational frequency in the final state for the new system is of the same order as that in the initial state of the older system, the difference between them is beyond the limits of observational error, and the two systems have no state in common. If, however, for both systems band-origin data were available instead of P-head coefficients only, it is possible that the two systems would be found to have the $^2P$ state of the doublet system $^2P \rightarrow {}^2S$ in common. While higher dispersion may be desirable in order to confirm the absence of other heads in the new bands, the apparently single nature of the P heads and the non-detection of the Q heads with the considerable dispersion employed appears to exclude a $^2S \rightarrow {}^2P$ transition and suggests a transition between two like states, *e.g.*, $^2P \rightarrow {}^2P$. The normal state of MgF is probably $^2S$ (the final state for the doublet system).

The present spectrograms of the new system show no evidence of the vibrational Mg-isotope effect. The line structure of the new bands is partially resolved, but considerably higher dispersion is necessary for the rotational quantum analysis of the new as well as of the older bands.

## DESCRIPTION OF PLATE 8.

FIGS. 1 and 2.—BeO in carbon arc in air: (*a*) Outer flame, yellow stage showing three sequences of the BeF band-system described in section 2; (*b*) outer flame, blue stage showing the new bands (oxide or fluoride, $BeF_2$ ?) described in section 4; the wave-lengths of some of the heads of the new bands are given.

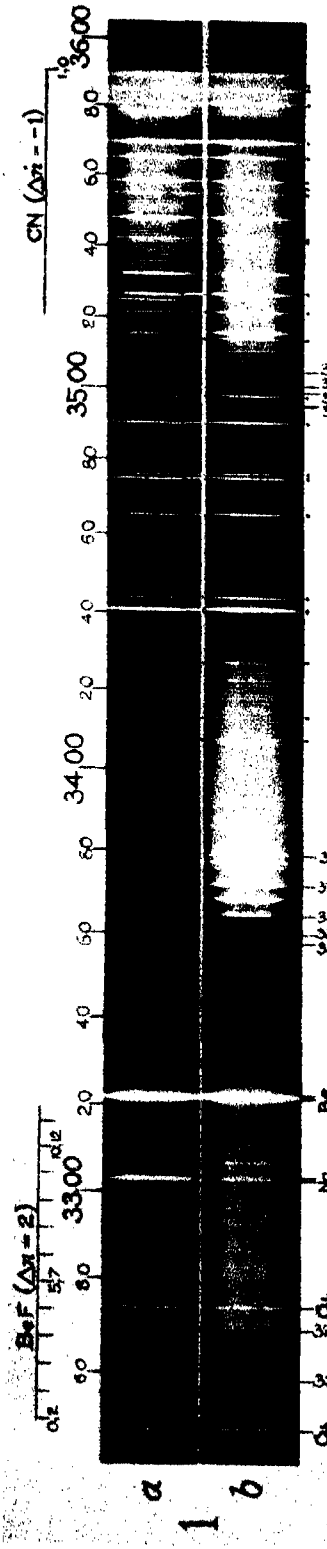
Lines of Fe, Be, Na, Cu and Al and the λ 3590 sequence of CN bands are common to (*a*) and (*b*).

FIG. 3.—$MgF_2$ in carbon arc in air: outer flame showing the new band-system of MgF described in section 6, and lines of Fe, Al and Pb. None of the strong Mg lines developed occur in the small range of wave-lengths in this reproduction.

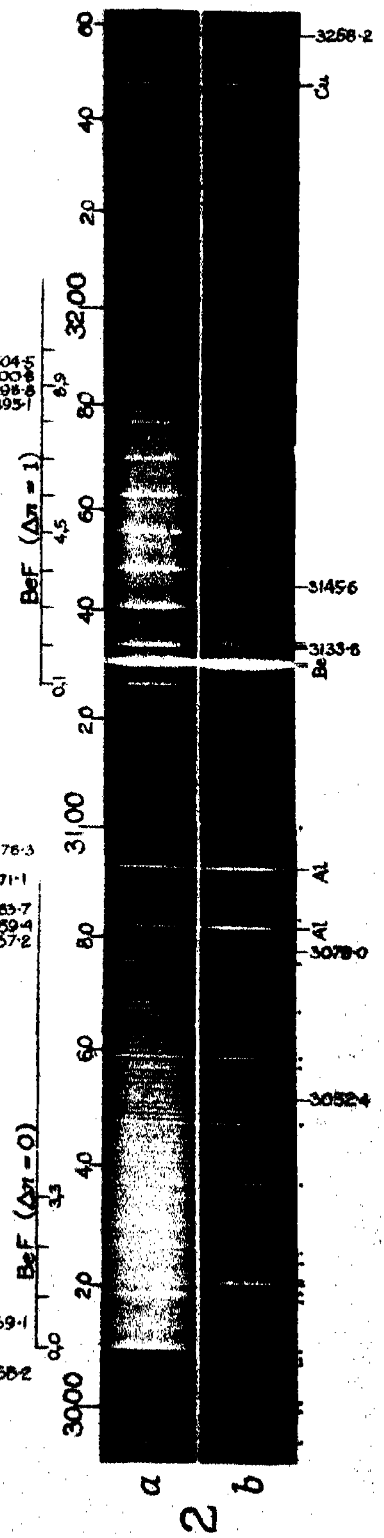
Lines of Fe are indicated by dots, and those of other metals by chemical symbols.

## 7. *Summary.*

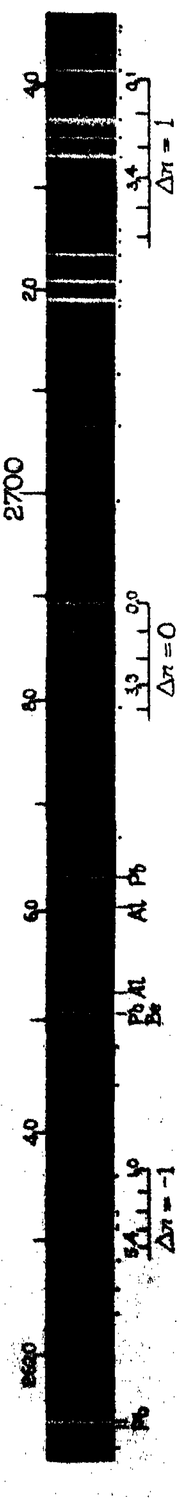
The vibrational analysis of the band-head data for the BeF doublet system leads to the following interpretation of the heads in each band, those in


CN (Δn = -1)
1,0
3600
8,0
6,0
4,0
2,0
3500
3504·5
3500·8
3498·8
3495·1
80
60
40
20
3400
80
3376·3
3371·1
3363·7
3359·4
3357·2
60
40
20
Be
Na
3300
BeF (Δn = 2)
0,12
5,7
0,2
80
Cu
3269·1
60
3258·2
Cu
BeF (Δn = 0)
3,3
0,0
a
b

1


80
3268·2
Cu
40
20
3200
BeF (Δn = 1)
8,9
4,5
0,1
80
60
40
3145·6
3133·6
Be
20
3100
Al
80
Al
3078·0
60
3052·4
40
20
3000
a
b

2


40
0,1
Δn = 1
3,4
20
2700
0,0
Δn = 0
3,3
80
Pb
60
Al
Pb
Al
Be
40
1,0
Δn = -1
5,4
2620
Pb

3

brackets not having yet been detected: $R_2$, $R_1$, $Q_2$, ($Q_1$) with a doublet separation of the order $R_2 - R_1 = 3$ cm.$^{-1}$, rather than $R_2$, $Q_2$, ($R_1$), $Q_1$ with a separation $Q_2 - Q_1 = 35$ cm.$^{-1}$ as hitherto assumed; see diagram on p. 216. With this interpretation there is now a continuous increase of the separation of the system-origins of the doublet systems of the alkaline earth fluorides from BeF to BaF, though its significance is not apparent as it is not yet certain that all these systems are due to analogous electronic transitions, *e.g.*, $^2P \rightarrow {}^2S$.

With BeO in the carbon arc in air conditions may be so arranged as to obtain in the outer flame either (*a*) the BeF system strong with the BeO system relatively weak, or (*b*) the BeO system strong with hardly a trace of the BeF system. In condition (*b*) the ultra-violet region λ 3500–λ 2900 (where the BeF system would occur if developed) is occupied by a new set of bands, which, like the BeF and BeO bands, are degraded towards the red. A similar result is obtained, though less satisfactorily, with other Be salts instead of BeO. The new bands are less regularly distributed than any bands of diatomic molecules, and are due either to $BeF_2$ or to an oxide of beryllium. No bands due to BeCl and no further bands of BeF have been found.

The data for the BeO band-system are extended by the recognition of a violet sequence $n'' - n' = -2$, not hitherto observed on account of the λ 4216 sequence of CN and strong metallic lines.

With $MgF_2$ in the carbon arc in air the outer flame develops, in addition to the MgF doublet system, a new ultra-violet system of three sequences of apparently single-headed bands degraded to the further ultra-violet. P-head data and $n'$, $n''$ values are given for the new system, which is due also to MgF, and may have for its final state the initial state for the doublet system. If $^2P \rightarrow {}^2S$ be assumed for the doublet system the new system may be $^2P \rightarrow {}^2P$.

The author has pleasure in thanking the Government Grant Committee of the Royal Society for the Hilger micrometer and the quartz prism and lens of the Littrow spectrograph used, and Prof. A. Fowler for a very helpful discussion of some questions raised in the course of this sequel to investigations carried out in his laboratory by Dr. L. C. Glaser and Dr. S. Datta.

# *The Tides in Oceans on a Rotating Globe.—Part* II.

By Prof. G. R. Goldsbrough, D.Sc., Armstrong College, Newcastle-on-Tyne.

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## *Introduction.*

§ 1. The method used in the previous paper* finds a ready application to certain cases of tidal waves in flat rotating seas. The first part of this paper discusses the case of a semi-circular basin in which the law of depth is $h_0(1-r^2/a^2)$ so that the bottom shelves from the centre to the circumferential edge. Complete results are given for a certain depth and the positions of the rotating nodal line, corresponding to the lowest normal mode, are shown in a diagram. The solution is expressed in terms of a certain type of hypergeometric function.

It is further shown that, by an extension of the same method, it is possible to solve the case of a sectorial basin of any angle with the same law of depth.

The process is also applied to the semi-circular basin of uniform depth. This problem has been completely solved by Proudman.† Proudman's method is shorter, but the present solution is worth including because of its analytical interest, though it has not been considered necessary to complete it.

## *The Case of a Plane Rotating Semi-Circular Basin of Variable Depth.*

§ 2. Consider a plane semi-circular sheet of water rotating with angular velocity $\omega$. In the usual notation,‡ the equations for the tidal vibrations expressed in polar co-ordinates are, on the removal of the usual time factor $e^{i\sigma t}$,

$$\left.\begin{aligned} \mathrm{R} &= \frac{g}{\sigma^2-4\omega^2}\left(\frac{\partial\zeta}{\partial r}-\frac{2i\omega}{\sigma r}\frac{\partial\zeta}{\partial\theta}\right), \\ \Theta &= \frac{ig}{\sigma^2-4\omega^2}\left(\frac{2\omega}{\sigma}\frac{\partial\zeta}{\partial r}-\frac{i}{r}\frac{\partial\zeta}{\partial\theta}\right), \\ -\zeta &= \frac{\partial(hr\mathrm{R})}{r\,\partial r}+\frac{\partial(h\Theta)}{r\,\partial\theta}. \end{aligned}\right\} \tag{1}$$

We shall choose, as the law of depth, $h = h_0(1-r^2/a^2)$ representing a basin of radius $a$ deepest at the centre and shelving towards the circumference.

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* 'Roy. Soc. Proc.,' A, vol. 117, p. 692 (1928).

† 'M.N.R.A.S.,' Geophysical Suppl., vol. 1, p. 360; vol. 2, p. 32.

‡ Lamb, 'Hydrodynamics,' 4th ed., p. 311.

If we substitute this value for $h$ in (1) and eliminate R and $\Theta$ we find the equation

$$\left(\frac{1-r^2}{a^2}\right)\left(\frac{\partial^2\zeta}{\partial r^2}+\frac{1}{r}\frac{\partial\zeta}{\partial r}+\frac{1}{r^2}\frac{\partial^2\zeta}{\partial\theta^2}\right)-\frac{2}{a^2}\left(r\frac{\partial\zeta}{\partial r}-\frac{2i\omega}{\sigma}\frac{\partial\zeta}{\partial\theta}\right)+\frac{\sigma^2-4\omega^2}{gh_0}\zeta=0. \quad (2)$$

It is convenient to reduce the equations by putting

$$\rho=r^2/a^2,\ \kappa^2=\frac{(\sigma^2-4\omega^2)\,a^2}{gh_0},$$

thus (2) and the second of equations (1) become

$$4\rho\,(1-\rho)\frac{\partial^2\zeta}{\partial\rho^2}+4\,(1-2\rho)\frac{\partial\zeta}{\partial\rho}+\frac{1-\rho}{\rho}\frac{\partial^2\zeta}{\partial\theta^2}+\kappa^2\zeta+\frac{4\iota\omega}{\sigma}\frac{\partial\zeta}{\partial\theta}=0. \quad (3i)$$

$$\Theta=\frac{\iota g}{\sigma^2-4\omega^2}\left(\frac{4\omega}{\sigma}\frac{\partial\zeta}{\partial\rho}-\frac{\iota}{\rho}\frac{\partial\zeta}{\partial\theta}\right). \quad (3ii)$$

Now assume $\zeta\propto e^{\iota s\theta}$, where $s$ is real but for the present unrestricted. Equation (3i) then becomes

$$4\rho\,(1-\rho)\frac{d^2\zeta}{d\rho^2}+4\,(1-2\rho)\frac{d\zeta}{d\rho}-\frac{(1-\rho)\,s^2\zeta}{\rho}+(\kappa^2-4\omega s/\sigma)\,\zeta=0. \quad (4)$$

This equation has a solution in the form of a power series in $\rho$ beginning with the term $\rho^{s/2}$. This series is convergent for values of $\rho<1$, but is divergent when $\rho=1$. For special values of $\kappa^2-4\omega s/\sigma$, however, the series terminates, and hence is available over the range $0\leqslant\rho\leqslant 1$. These special values, however, amount to a determination of either $\sigma$ or $s$, and neither choice is convenient at this stage.

In (4) put $\zeta=\rho^{s/2}\mathrm{X}$, and we then have

$$\rho\,(1-\rho)\,\mathrm{X}''+\{(s+1)-p\,(s+2)\}\,\mathrm{X}'+\tfrac{1}{4}\,(\kappa^2-2s-4ws/\sigma)\,\mathrm{X}=0. \quad (5)$$

Now consider a similar equation

$$\rho\,(1-\rho)\,\mathrm{X}''+\{(s+1)-\rho\,(s+2)\}\,\mathrm{X}'+u\,(u+s+1)\,\mathrm{X}=0 \quad (6)$$

This equation is satisfied by

$$\mathrm{X}=\mathrm{X}_n^s=\mathrm{F}\,(s+n+1,\ -n,\ s+1,\ \rho),$$

where F is the hypergeometric function.

Further, the series for F is not convergent for $\rho=1$, but when $n$ is a positive integer it terminates. $\mathrm{X}_n^s$ is then a solution of (6) valid over the range $0\leqslant\rho\leqslant 1$ for all positive values of $s$ provided $n$ is a positive integer.

§ 3. The functions $\mathrm{X}_n^s$ are a particular case of certain functions of the form $\mathrm{F}\,(\alpha+n,\ -n,\ \gamma,\ x)$ which have been studied at length by Darboux.*

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* 'J. des Math.,' vol. 3, p. 377 (1878); see also Courant und Hilbert, 'Methoden der Mathematischen Physik,' vol. 1, p. 74.

By putting $\gamma = \alpha = s + 1$ in his results, we may deduce the corresponding results for the functions $X_n^s$. We have, then, the following :

$$X_n^s = F(s + n + 1, -n, s + 1, \rho)$$

$$= \frac{\rho^{-s}}{(s + 1)(s + 2) \ldots (s + n)} \frac{d^n}{d\rho^n} \{\rho^{s+n}(1 - \rho)^n\}. \tag{7}$$

From (5) it may be quickly deduced that

$$\int_0^1 \rho^s X_n^s X_m^s \, d\rho = 0, \text{ if } m \neq n, \text{ and } s + 1 > 0. \tag{8}$$

And from (5) with the aid of (7), it follows that

$$\int_0^1 \rho^s (X_n^s)^2 \, d\rho = \frac{1}{s + 2n + 1} \frac{\Gamma^2(n + 1)\,\Gamma^2(s + 1)}{\Gamma^2(s + n + 1)}. \tag{9}$$

From (8) and (9) it is evident that the sequence of functions $X_n^s$ ($n$ any integer) may, on dividing each term by a suitable factor, be made a normal sequence.

Darboux has further shown that under suitable restrictions any arbitrary function of $\rho$ may be expanded in a series, valid from $\rho = 0$ to $\rho = 1$, of the form,

$$f(\rho) = \sum_n A_n^s X_n^s(\rho),$$

where

$$A_n^s = \int_0^1 \rho^s f(\rho)\, X_n^s(\rho)\, d\rho \div \frac{\Gamma^2(n + 1)\,\Gamma^2(s + 1)}{(s + 2n + 1)\,\Gamma^2(s + n + 1)}. \tag{10}$$

In particular, $\rho^p$ can be expanded in this way for any positive value of $p$, and for any negative value of $p$ provided that $|p| < s/2 + \frac{1}{2}$. In the special case where $p$ is a positive integer, the series is finite. Applying the formula (10) we find, subject to the condition stated,

$$\rho^p = \sum_n A_n^s X_n^s,$$

$$A_n^s = (-1)^n \frac{p(p-1)\ldots(p-n+1)}{n\,!} \frac{\Gamma(s+n+1)\,\Gamma(p+s+1)(2n+s+1)}{\Gamma(s+1)\,\Gamma(s+n+p+2)}. \tag{11}$$

From the form of the equation (4) which is that requiring solution, it is evident that the functions appearing will not be $X_n^s$, but $\rho^{s/2} X_n^s$. Multiplying the series in (11) by $\rho^{s/2}$, we have

$$\rho^{p+s/2} = \sum_n A_n^s \rho^{s/2} X_n^s;$$

or

$$\rho^{\nu} = \sum_n A_n^s \rho^{s/2} X_n^s, \tag{12}$$

where $\nu = p + s/2$.

If $(\nu - s/2)$ is positive, the expansion (12) is valid, from what has gone before. Let $\nu - s/2$ be negative and equal to $-q$. Then $q < s/2 + \frac{3}{4}$, for the expansion to be valid. Put $q = s/2 + \frac{3}{4} - \varepsilon$, where $\varepsilon$ is positive. Then we must have $\nu - s/2 = -s/2 - \frac{3}{4} + \varepsilon$, or $\nu = \varepsilon - \frac{3}{4}$. Hence the expansion in (12) will hold for all values of $\nu$ greater than $-\frac{3}{4}$.*

It is of some interest to write out the forms of the earlier of functions $X_n^s$. They are

$$X_0^s = 1,$$

$$X_1^s = 1 - \binom{1}{1}\frac{s+2}{s+1}\rho,$$

$$X_2^s = 1 - \binom{2}{1}\frac{s+3}{s+1}\rho + \binom{2}{2}\frac{(s+3)(s+4)}{(s+1)(s+2)}\rho^2,$$

$$X_3^s = 1 - \binom{3}{1}\frac{s+3}{s+1}\rho + \binom{3}{2}\frac{(s+4)(s+5)}{(s+1)(s+2)}\rho^2 - \binom{3}{3}\frac{(s+4)(s+5)(s+6)}{(s+1)(s+2)(s+3)}\rho^3,$$

. . . . . . . . . . . . . . . . . . . . . . . .

$$X_n^s = 1 + \sum_r (-1)^r \rho^r \binom{n}{r}\frac{(s+n+1)(s+n+2)\dots(s+n+r)}{(s+1)(s+2)\dots(s+r)}.$$

It is also to be noted that the coefficient $A_n^s$ in the expansion of $\rho^{\nu/2}$ as given in (12) may be written in the form

$$A_n^s(\nu) = (-1)^n \frac{\left(\frac{\nu-s}{2}\right)\left(\frac{\nu-s}{2}-1\right)\dots\left(\frac{\nu-s}{2}-n+1\right)}{n\,!}(2n+s+1)$$
$$\times \frac{\Gamma(s+n+1)\,\Gamma\left(\frac{\nu+s}{2}+1\right)}{\Gamma(s+1)\,\Gamma\left(\frac{\nu+s}{2}+n+2\right)}. \qquad (13)$$

§ 4. We can now proceed to form the requisite null functions, following the method of the previous paper.†

In the range $0 < \theta < \pi$, we have the expansion

$$\sin s\theta = \frac{4s}{\pi}\sum_n \frac{1}{s^2 - n^2}\cos n\theta,$$

where $s = 1, 2, 3, \dots, s - n$ is odd, and when $n = 0$, $s$ being odd, the coefficient is $2/s\pi$.

The expansion may be written

$$e^{\iota s\theta} - e^{-\iota s\theta} - \frac{4s\iota}{\pi}\sum_n \frac{1}{s^2 - n^2}(e^{\iota n\theta} + e^{-\iota n\theta}) = 0. \qquad (14)$$

---

* Throughout it is assumed, as already stated, that $s + 1 > 0$.

† *Loc. cit.*, p. 702.

Hence taking arbitrary multipliers $E_s$, we have

$$\sum_s E_s\left\{(e^{is\theta}-e^{-is\theta})-\frac{4si}{\pi}\sum_n\frac{1}{s^2-n^2}(e^{in\theta}+e^{-in\theta})\right\}=0, \qquad (14')$$

for all values of $\theta$ in the range.

Now multiply through in (14) by $\rho^{s/2}$, replacing it in the latter terms by $\sum_\nu A_\nu^n(s)\,X_\nu^n\,\rho^{n/2}$, as derived from (13).* On summing again as in (14′) we have

$$\sum_s E_s\left\{\rho^{s/2}(e^{is\theta}-e^{-is\theta})-\frac{4s\iota}{\pi}\sum_n\frac{1}{s^2-n^2}(e^{in\theta}+e^{-in\theta})\,.\,\rho^{n/2}\sum_\nu A_\nu^n(s)\,X_\nu^n\right\}=0, (15)$$

for $0<\theta<\pi$ and $0\leqslant\rho\leqslant 1$.

The operator of the left member of equation (3) is

$$4\rho(1-\rho)\frac{\partial^2}{\partial\rho^2}+4(1-2\rho)\frac{\partial}{\partial\rho}+\frac{1-\rho}{\rho}\frac{\partial^2}{\partial\theta^2}+\frac{4\iota\omega}{\sigma}\frac{\partial}{\partial\theta}+\kappa^2.$$

If we apply this operator to a typical term of (15), such as $\rho^{n/2}X_\nu^n e^{in\theta}$, the result is

$$\{\kappa^2-4\omega n/\sigma-2n-4\nu(n+\nu+1)\}\,\rho^{n/2}X_\nu^n e^{in\theta}\,; \qquad (16)$$

while the operation upon $\rho^{n/2}X_\nu^n e^{-in\theta}$ gives the result

$$\{\kappa^2+4\omega n/\sigma-2n-4\nu(n+\nu+1)\}\,e^{n/2}X_\nu^n e^{-in\theta}. \qquad (17)$$

We now take

$$\begin{aligned}\zeta=\sum_s E_s\Bigg[&\frac{\rho^{s/2}e^{is\theta}}{\kappa^2-4\omega s/\sigma-2s}-\frac{\rho^{s/2}e^{-is\theta}}{\kappa^2+4\omega s/\sigma-2s}\\&-\frac{4s\iota}{\pi}\sum_n\frac{1}{s^2-n^2}\sum_\nu\Bigg\{\frac{\rho^{n/2}A_\nu^n(s)\,X_\nu^n\,e^{in\theta}}{\kappa^2-4\omega n/\sigma-2n-4\nu(n+\nu+1)}\\&\qquad+\frac{\rho^{n/2}A_\nu^n(s)X_\nu^n\,e^{-in\theta}}{\kappa^2+4\omega n/\sigma-2n-4\nu(n+\nu+1)}\Bigg\}\Bigg]. \qquad (18)\end{aligned}$$

On substituting this value of $\zeta$ in the left member of (3i), the result, by (16) and (17), is

$$\sum_s E_s\left\{\rho^{s/2}(e^{is\theta}-e^{-is\theta})-\frac{4si}{\pi}\sum_n\frac{1}{s^2-n^2}(e^{in\theta}+e^{-in\theta})\,\rho^{n/2}\sum_\nu A_\nu^n(s)\,X_\nu^n\right\},$$

and this by (15) is zero.

The expression in (18) then satisfies (3i) for all values of $E_s$; the cofactor of each E is convergent throughout the area of the semi-circle and finite in value at the boundary $\rho = 1$; and there is an infinite number of undetermined constants E which can be chosen so as to satisfy the one remaining condition, *i.e.*, the condition that the velocity across the boundaries $\theta = 0, \pi$ is zero. It therefore is the required form of solution for the problem in hand.

---

* The parameter $s$ in $A_\nu^n(s)$ is indicated to show the derivation of the coefficient.

§ 5. The following table gives the values of the coefficients $A_r^n(s)$ for various values of the arguments, the numbers of terms in each series being enough for our purpose :—

| | | | | |
|---|---|---|---|---|
| | | $n = 0.$ | $n = 2.$ | $n = 4.$ |
| $s = 1.$ | $A_0^n$ | $\frac{2}{3}$ | $\frac{6}{5}$ | $\frac{10}{7}$ |
| | $A_1^n$ | $-\frac{2}{5}$ | $\frac{6}{7}$ | $\frac{10}{3}$ |
| | $A_2^n$ | $-\frac{2}{21}$ | $\frac{4}{5}$ | $\frac{450}{77}$ |
| | $A_3^n$ | $-\frac{2}{45}$ | $\frac{20}{77}$ | $\frac{350}{39}$ |
| | | $n = 0.$ | $n = 2.$ | $n = 4.$ |
| $s = 3.$ | $A_0^n$ | $\frac{2}{5}$ | $\frac{6}{7}$ | $\frac{10}{9}$ |
| | $A_1^n$ | $-\frac{18}{35}$ | $-\frac{10}{21}$ | $\frac{80}{99}$ |
| | $A_2^n$ | $\frac{2}{21}$ | $-\frac{4}{33}$ | $\frac{100}{143}$ |
| | $A_3^n$ | $\frac{2}{165}$ | $-\frac{15}{143}$ | $\frac{280}{429}$ |
| | | $n = 1.$ | $n = 3.$ | $n = 5.$ |
| $s = 2.$ | $A_0^n$ | $\frac{4}{5}$ | $\frac{8}{7}$ | $\frac{4}{3}$ |
| | $A_1^n$ | $-\frac{16}{35}$ | $\frac{16}{21}$ | $\frac{32}{11}$ |
| | $A_2^n$ | $-\frac{4}{35}$ | $\frac{160}{231}$ | $\frac{700}{143}$ |
| | $A_3^n$ | $-\frac{64}{1155}$ | $\frac{2000}{3003}$ | $\frac{3136}{2145}$ |
| $s = 4.$ | $A_0^n$ | $\frac{4}{7}$ | $\frac{8}{9}$ | $\frac{12}{11}$ |
| | $A_1^n$ | $-\frac{16}{21}$ | $-\frac{16}{33}$ | $\frac{96}{143}$ |
| | $A_2^n$ | $\frac{12}{77}$ | $-\frac{160}{1287}$ | $\frac{168}{143}$ |
| | $A_3^n$ | $\frac{64}{3003}$ | $-\frac{80}{1287}$ | $\frac{1344}{2431}$ |

The condition that determines the quantities E is that $\Theta = 0$ when $\theta = 0, \pi$. From (3ii) this requires that $\left(\frac{4\omega}{\sigma} \cdot \rho \frac{\partial}{\partial \rho} - \iota \frac{\partial}{\partial \theta}\right) \zeta = 0$ at $\theta = 0, \pi$. Putting

$f = \sigma/2\omega$ we have

$$
\begin{aligned}
&\left(\frac{2\rho}{f}\frac{\partial}{\partial\rho} - \iota\frac{\partial}{\partial\theta}\right)\zeta \\
&= \sum_s \mathrm{E}_s \Bigg[ \frac{\left(\frac{1}{f}+1\right) s\rho^{s/2} e^{\iota s\theta}}{\kappa^2 - 2s/f - 2s} - \frac{\left(\frac{1}{f}-1\right) s\rho^{s/2} e^{-\iota s\theta}}{\kappa^2 + 2s/f - 2s} \\
&\qquad - \frac{4s\iota}{\pi}\sum_n \frac{1}{s^2-n^2}\Bigg\{\sum_\nu \frac{e^{\iota n\theta}\,.\,\mathrm{A}^n_\nu(s)}{\kappa^2 - 2n/f - 2n - 4\nu(n+\nu+1)} \\
&\qquad\qquad \left(n\rho^{n/2}\left(\frac{1}{f}+1\right) + \sum_r (-1)^r \rho^{r+n/2}\left(\frac{2r+n}{f}+n\right)\binom{\nu}{r} \frac{(n+\nu+1)\ldots(\nu+n+r)}{(n+1)\ldots(n+r)}\right) \\
&\qquad - \sum_\nu \frac{e^{-\iota n\theta}\mathrm{A}^n_\nu(s)}{\kappa^2 + 2n/f - 2n - 4\nu(n+\nu+1)} \\
&\qquad\qquad \left(n\rho^{n/2}\left(\frac{1}{f}-1\right) + \sum_r (-1)^r \rho^{r+n/2}\left(\frac{2r+n}{f}-n\right)\binom{\nu}{r} \frac{(n+\nu+1)\ldots(n+\nu+r)}{(n+1)\ldots(n+r)}\right)\Bigg\}\Bigg] \\
&= \sum_s \mathrm{E}_s \Bigg[ \frac{\left(\frac{1}{f}+1\right) s\rho^{s/2} e^{\iota s\theta}}{\kappa^2 - 2s/f - 2s} - \frac{\left(\frac{1}{f}-1\right) s\rho^{s/2} e^{-\iota s\theta}}{\kappa^2 + 2s/f - 2s} \\
&\qquad - \frac{4s\iota}{\pi}\sum_n \frac{1}{s^2-n^2} e^{\iota n\theta}\rho^{n/2}\sum_\nu \mathrm{B}^n_\nu(s)\,\rho^\nu \\
&\qquad - \frac{4s\iota}{\pi}\sum_n \frac{1}{s^2-n^2} e^{-\iota n\theta}\rho^{n/2}\sum_\nu \mathrm{B}^{-n}_\nu(s)\,\rho^\nu \Bigg], \qquad (19)
\end{aligned}
$$

where the coefficients $\mathrm{B}^n_\nu(s)$ and $\mathrm{B}^{-n}_\nu(s)$ can be determined from the series quoted.* For example

$$
\begin{aligned}
\mathrm{B}^n_0(s) &= n\left(\frac{1}{f}+1\right)\left\{\frac{\mathrm{A}^n_0(s)}{\kappa^2 - 2n/f - 2n} + \frac{\mathrm{A}^n_1(s)}{\kappa^2 - 2n/f - 2n - 4(n+2)} \right. \\
&\qquad \left. + \frac{\mathrm{A}^n_2(s)}{\kappa^2 - 2n/f - 2n - 8(n+3)} + \ldots\right\}, \\
\mathrm{B}^n_1(s) &= -\left(\frac{2+n}{f}+n\right)\left\{\frac{\frac{n+2}{n+1}\mathrm{A}^n_1(s)}{\kappa^2 - 2n/f - 2n - 4(n+2)} \right. \\
&\qquad \left. + \frac{\frac{2(n+3}{n+1}\mathrm{A}^n_2(s)}{\kappa^2 - 2n/f - 2n - 8(n+3)} + \frac{\frac{3(n+4)}{n+1}\,.\,\mathrm{A}^n_3(s)}{\kappa^2 - 2n/f - 2n - 12(n+4)}\ldots\right\},
\end{aligned}
$$

---

* It is assumed that the re-arrangement of the series in this way is permissible.

$$\mathrm{B}_2^n(s) = \left(\frac{4+n}{f}+n\right)\left\{\frac{\dfrac{(n+3)(n+4)}{(n+1)(n+2)}\mathrm{A}_2^n(s)}{\kappa^2-2n/f-2n-8(n+3)}\right.$$

$$\left.+\frac{\dfrac{3(n+4)(n+5)}{(n+1)(n+2)}\mathrm{A}_3^n(s)}{\kappa^2-2n/f-2n-12(n+4)}+\dots\right\},$$

and so on.

On equating the expression on the right of (19) to zero when $\theta = 0$ and when $\theta = \pi$ we find,

$$\left.\begin{aligned}
&\sum^{s\ \text{odd}}\mathrm{E}_s\left\{\frac{s\left(\dfrac{1}{f}+1\right)\rho^{s/2}}{\kappa^2-2s/f-2s}-\frac{s\left(\dfrac{1}{f}-1\right)\rho^{s/2}}{\kappa^2+2s/f-2s}\right\}\\
&\qquad-\sum^{s\ \text{even}}\mathrm{E}_s\frac{4si}{\pi}\left\{\sum^{n\ \text{odd}}\frac{1}{s^2-n^2}\rho^{n/2}\sum_{\nu}\left[\mathrm{B}_\nu^n(s)+\mathrm{B}_\nu^{-n}(s)\right]\rho^\nu\right\}=0,\\
&\sum^{s\ \text{even}}\mathrm{E}_s\left\{\frac{s\left(\dfrac{1}{f}+1\right)\rho^{s/2}}{\kappa^2-2s/f-2s}-\frac{s\left(\dfrac{1}{f}-1\right)\rho^{s/2}}{\kappa^2+2s/f-2s}\right\}\\
&\qquad-\sum^{s\ \text{odd}}\mathrm{E}_s\frac{4si}{\pi}\left\{\sum^{n\ \text{even}}\frac{1}{s^2-n^2}\rho^{n/2}\sum_{\nu}\left[\mathrm{B}_\nu^n(s)+\mathrm{B}_\nu^{-n}(s)\right]\rho^\nu\right\}=0.
\end{aligned}\right\}. \quad (20)$$

We now equate to zero coefficients of $\rho^{1/2}$, $\rho^1$, $\rho^{3/2}$ ..., and have the following equations :

$$\left.\begin{aligned}
&\mathrm{E}_1\left\{\frac{\dfrac{1}{f}+1}{\kappa^2-2/f-2}-\frac{\dfrac{1}{f}-1}{\kappa^2+2/f-2}\right\}\\
&-\mathrm{E}_2\cdot\frac{8i/\pi}{2^2-1^2}\left[\mathrm{B}_0^1(2)+\mathrm{B}_0^{-1}(2)\right]-\mathrm{E}_4\frac{16i}{\pi}\\
&\qquad\qquad\times\frac{1}{4^2-1^2}\left[\mathrm{B}_0^1(4)+\mathrm{B}_0^{-1}(4)\right]\dots=0\\
&\mathrm{E}_3\left\{\frac{3\left(\dfrac{1}{f}+1\right)}{\kappa^2-6/f-6}-\frac{3\left(\dfrac{1}{f}-1\right)}{\kappa^2+6/f-6}\right\}\\
&-\mathrm{E}_2\left\{\frac{8i/\pi}{2^2-3^2}\left[\mathrm{B}_0^3(2)+\mathrm{B}_0^{-3}(2)\right]+\frac{8i/\pi}{2^2-1^2}\left[\mathrm{B}_1^1(2)+\mathrm{B}_1^{-1}(2)\right]\right\}\\
&-\mathrm{E}_4\left\{\frac{16i/\pi}{4^2-3^2}\left[\mathrm{B}_0^3(4)+\mathrm{B}_0^{-3}(4)\right]+\frac{16i/\pi}{4^2-1^2}\left[\mathrm{B}_1^1(4)+\mathrm{B}_1^{-1}(4)\right]\right\}\dots=0,\\
&\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad\cdot
\end{aligned}\right|$$

$$\left.\begin{aligned}
&\mathrm{E}_2\left\{\frac{2\left(\frac{1}{f}+1\right)}{\kappa^2-4/f-4}-\frac{2\left(\frac{1}{f}-1\right)}{\kappa^2+4/f-4}\right\}\\
&-\mathrm{E}_1\frac{4\iota}{\pi}\left\{\frac{1}{1^2}\cdot\mathrm{B}_1^0(1)+\frac{1}{1^2-2^2}[\mathrm{B}_0^2(1)+\mathrm{B}_0^{-2}(1)]\right\}\\
&-\mathrm{E}_3\frac{12\iota}{\pi}\left\{\frac{1}{3^2}\mathrm{B}_1^0(3)+\frac{1}{3^2-2^2}[\mathrm{B}_0^2(3)+\mathrm{B}_0^{-2}(3)]\right\}\ldots=0,\\
&\mathrm{E}_4\left\{\frac{4\left(\frac{1}{f}+1\right)}{\kappa^2-8/f-8}-\frac{4\left(\frac{1}{f}-1\right)}{\kappa^2+8/f-8}\right\}\\
&-\mathrm{E}_1\frac{4\iota}{\pi}\left\{\frac{1}{1^2}\mathrm{B}_2^0(1)+\frac{1}{1^2-2^2}[\mathrm{B}_1^2(1)+\mathrm{B}_1^{-2}(1)]\right.\\
&\qquad\qquad\left.+\frac{1}{1^2-4^2}[\mathrm{B}_0^4(1)+\mathrm{B}_0^{-4}(1)]\right\}\\
&-\mathrm{E}_3\frac{12\iota}{\pi}\left\{\frac{1}{3^2}\mathrm{B}_2^0(3)+\frac{1}{3^2-2^2}[\mathrm{B}_1^2(3)+\mathrm{B}_1^{-2}(3)]\right.\\
&\qquad\qquad\left.+\frac{1}{3^2-4^2}[\mathrm{B}_0^4(3)+\mathrm{B}_0^{-4}(3)]\right\}\ldots=0\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots
\end{aligned}\right\},\quad(21)$$

The eliminant of the E's in (21) will give an equation which will determine the period of the free normal modes of oscillation, $2\pi/\sigma$. In order to proceed to numerical values we must take a value for the depth. The mean depth, in the case of a basin such as we have prescribed, is one-half of the maximum depth $h_0$. Now

$$\kappa^2=(\sigma^2-4\omega^2)\,a^2/gh_0=(f^2-1)\,4\omega^2a^2/gh_0=(f^2-1)\,4a^2\,\Omega^2\sin^2\lambda/gh_0$$

where $\Omega$ is the earth's angular velocity and $\lambda$ is the latitude of the basin. The dimensions of the basin are supposed to be such that the variation in $\lambda$ may be neglected. For the Black Sea,* $4a^2\,\Omega^2\sin^2\lambda/gh_0=0\cdot112$, and we shall use this figure to determine the lowest free period of oscillation of a semicircular basin comparable with the Black Sea and for which the law of depth is that chosen here.

§ 6. The first few rows and columns of the determinant of (21) are

$$\begin{array}{ccc}
\Phi_{11}, & \Phi_{12}, & \Phi_{13},\\
\Phi_{21}, & \Phi_{22}, & \Phi_{23},\\
\Phi_{31}, & \Phi_{32}, & \Phi_{33},
\end{array}$$

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* Proudman, 'M.N.R.A.S.,' Geophysical suppl., vol. II, p. 42.

where

$$\Phi_{11} = \frac{1/f}{0\cdot112\,(f-1)-2/f} - \frac{1/f}{-0\cdot112\,(f+1)+2/f},$$

$$\Phi_{12} = \frac{-8/\pi}{2^2-1^2}[\mathrm{B}_0^1(2)+\mathrm{B}_0^{-1}(2)],$$

$$\Phi_{13} = 0,$$

$$\Phi_{21} = \frac{4}{\pi}\left\{\mathrm{B}_1^0(1)+\frac{1}{1^2-2^2}[\mathrm{B}_0^2(1)+\mathrm{B}_0^{-2}(1)]\right\},$$

$$\Phi_{22} = \frac{2/f}{0\cdot112\,(f-1)-4/f} - \frac{2/f}{-0\cdot112\,(f+1)+4/f},$$

$$\Phi_{23} = \frac{12}{\pi}\left\{\frac{1}{3^2}\mathrm{B}_1^0(3)+\frac{1}{3^2-2^2}[\mathrm{B}_0^2(3)+\mathrm{B}_0^{-2}(3)]\right\},$$

$$\Phi_{31} = 0,$$

$$\Phi_{32} = -\frac{8/\pi}{2^2-3^2}[\mathrm{B}_0^3(2)+\mathrm{B}_0^{-3}(2)] - \frac{8/\pi}{2^2-1^2}[\mathrm{B}_1^1(2)+\mathrm{B}_1^{-1}(2)].$$

$$\Phi_{33} = \frac{3/f}{0\cdot112\,(f-1)-6/f} - \frac{3/f}{-0\cdot112\,(f+1)+6/f}.$$

If we take the first term only, the value of $f$ to make it vanish is $4\cdot22$.

Next consider two rows and columns, using $f = 4\cdot22$ in all but the first term. We find

$$\mathrm{B}_0^1(2) = -1\cdot640, \qquad \mathrm{B}_0^{-1}(2) = -1\cdot717, \qquad \mathrm{B}_1^0(1) = -0\cdot0798,$$

$$\mathrm{B}_0^2(1) = -1\cdot138, \qquad \mathrm{B}_0^{-2}(1) = -0\cdot337.$$

Hence

$$\frac{1}{f}\left\{\frac{1}{0\cdot112\,(f-1)-2/f} - \frac{1}{-0\cdot112\,(f+1)+2/f}\right\} = +0\cdot454,$$

and the value of $f$ derived from this is $4\cdot17$. Taking now three rows and columns, and evaluating the new terms using $f = 4\cdot17$, we find

$$\mathrm{B}_0^3(2) = -0\cdot946, \qquad \mathrm{B}_0^{-3}(2) = 1\cdot086, \qquad \mathrm{B}_1^1(2) = -0\cdot130,$$

$$\mathrm{B}_1^{-1}(2) = 0\cdot023, \qquad \mathrm{B}_1^0(3) = -0\cdot066, \qquad \mathrm{B}_0^2(3) = -0\cdot611,$$

$$\mathrm{B}_0^{-2}(3) = 1\cdot040.$$

From these

$$\frac{1}{f}\left\{\frac{1}{0\cdot112\,(f-1)-2/f} - \frac{1}{-0\cdot112\,(f+1)+2/f}\right\} = 0\cdot461.$$

This gives again $f = 4\cdot17$.

We may regard $4\cdot17$ as a close approximation to the value of the lowest root of the determinant. This value is near to $3\cdot87$, the value found by

Proudman for the corresponding case with uniform depth the same as the mean depth of this case.

Leaving $E_1$ arbitrary, and using the value of $f$ just found, we may calculate the remaining coefficients E. They are

$$E_2 = 0 \cdot 162\, E_1\, i,$$
$$E_3 = -0 \cdot 018\, E_1,$$
$$E_4 = 0 \cdot 002\, E_1\, i, \ldots .$$

Finally, on substituting these values and reducing, we have the complete value of $\zeta$, less an arbitrary factor, in the form

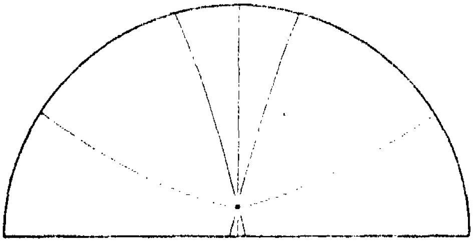
$$\begin{aligned}\zeta e^{-\iota\sigma\tau} = {} & \rho^{1/2} e^{\iota\theta} \{-1 \cdot 683 + 0 \cdot 0052\, X_1^1 + 0 \cdot 0005\, X_2^1 + 0 \cdot 0001\, X_3^1 \ldots\} \\ & + \rho^{1/2} e^{-\iota\theta} \{-2 \cdot 965 + 0 \cdot 0055\, X_1^1 + 0 \cdot 0005\, X_2^1 + 0 \cdot 0001\, X_3^1 \ldots\} \\ & + \rho^{3/2} e^{3\iota\theta} \{0 \cdot 020 + 0 \cdot 0024\, X_1^3 + 0 \cdot 0011\, X_2^3 + 0 \cdot 0006\, X_3^3 \ldots\} \\ & + \rho^{3/2} e^{-3\iota\theta} \{0 \cdot 027 + 0 \cdot 0028\, X_1^3 + 0 \cdot 0011\, X_2^3 + 0 \cdot 0006\, X_3^3 \ldots\} \\ & + i \{-0 \cdot 465 - 0 \cdot 082\, X_1^0 - 0 \cdot 0055\, X_2^0 - 0 \cdot 0012\, X_3^0 \ldots\} \\ & + i\rho e^{2\iota\theta} \{-0 \cdot 219 - 0 \cdot 0196\, X_1^2 - 0 \cdot 0078\, X_2^2 - 0 \cdot 0015\, X_3^2 \ldots\} \\ & + i\rho e^{-2\iota\theta} \{-0 \cdot 285 - 0 \cdot 0174\, X_1^2 - 0 \cdot 0082\, X_2^2 - 0 \cdot 0015\, X_3^2 \ldots\} \\ & + i\rho^2 e^{4\iota\theta} \{-0 \cdot 0123 - 0 \cdot 0086\, X_1^4 - 0 \cdot 0077\, X_2^4 - 0 \cdot 0073\, X_3^4 \ldots\} \\ & + i\rho^2 e^{-4\iota\theta} \{-0 \cdot 0342 - 0 \cdot 0098\, X_1^4 - 0 \cdot 0073\, X_2^4 - 0 \cdot 0076\, X_3^4 \ldots\}\end{aligned} \tag{22}$$

To see how far the velocity condition is satisfied by the solution (22) we can apply the operation $\left(\frac{2\rho}{f}\frac{\partial}{\partial\rho} - i\frac{\partial}{\partial\theta}\right)$ directly to it. From the form it is clear that after the operation has been performed the sums of the coefficients of the odd powers of $e^{\pm\iota\theta}$ and the even powers of $e^{\pm\iota\theta}$ must be separately zero for all values of $\rho$ from 0 to 1. At $\rho = 0$ the results are obviously zero. At the other points we have

| | Odd terms. | Even terms. |
|---|---|---|
| $\rho = \frac{1}{2}$: | $+2 \cdot 143 - 2 \cdot 058$, | $+0 \cdot 410 - 0 \cdot 426$. |
| $\rho = 1$: | $+3 \cdot 088 - 2 \cdot 971$, | $+0 \cdot 955 - 0 \cdot 948$. |

Considering the elaborate nature of the operations, these results are satisfactory.

The diagram below shows the position of the nodal line of this (the lowest) free mode at intervals of $\pi/4\sigma$. The amphidromic point occurs on the central radius at a distance of 0·12 of the radius from the centre of the semi-circle. The nodal line rotates in the same direction as the basin.



§ 7. The method of the previous sections is readily extended to include a system of forced tides. In equations (1) we replace $\zeta$ in R and $\Theta$ by $\zeta'$, $= \zeta - \bar{\zeta}$, where $g\bar{\zeta}$ is the tide producing potential. For a basin of small extent, $\bar{\zeta}$ has the known form $(\mathrm{A}\rho^{\frac{1}{2}}e^{\iota\theta} + \mathrm{B}\rho^{\frac{1}{2}}e^{-\iota\theta})\, e^{\iota\sigma t}$.* In this more general case, instead of (3i) we have

$$4\rho(1-\rho)\frac{\partial^2\zeta'}{\partial\rho^2} + 4(1-2\rho)\frac{\partial\zeta'}{\partial\rho} + \frac{1-\rho}{\rho}\frac{\partial^2\zeta'}{\partial\theta^2} + \frac{4\iota\omega}{\sigma}\frac{\partial\zeta'}{\partial\theta} + \kappa^2\zeta' = -\kappa^2\bar{\zeta}.$$

Owing to the presence of the right member in this equation we take for $\zeta'$ the same form as for $\zeta$ in (18) together with the two additional particular integrals

$$-\frac{\kappa^2 \mathrm{A}\rho^{\frac{1}{2}}e^{\iota\theta}}{\kappa^2 - 4\omega/\sigma - 2} - \frac{\kappa^2 \mathrm{B}\rho^{\frac{1}{2}}e^{-\iota\theta}}{\kappa^2 + 4\omega/\sigma - 2}.$$

The application of the boundary condition proceeds as before resulting in the set of equations (21) with certain right-hand members. The quantity $\sigma$ being in this case known, these equations completely determine the unknown coefficients $\mathrm{E}_s$.

§ 8. The method of the previous sections can also be easily extended to include the case of a sector of any angle with the same law of depth. We proceed to outline the process.

Let the sector have an angle $\alpha$. Then in place of the expansion (13) we take

$$e^{\iota s'\pi\theta/\alpha} - e^{-\iota s'\pi\theta/\alpha} - \frac{4s'\iota}{\pi}\sum_{n'}\frac{1}{s'^2 - n'^2}\left(e^{\iota n'\pi\theta/\alpha} + e^{-\iota n'\pi\theta/\alpha}\right) = 0, \qquad (13\mathrm{A})$$

$s'$, $n'$ being integers and $s' - n'$ odd.

If we write for convenience $s$, $n$ in place of $s'\pi/\alpha$, $n'\pi/\alpha$, we can form a null function in exactly the same way as before, as all the required conditions relating to the expansions are fulfilled. We then have in place of (15)

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* Proudman, 'M.N.R.A.S.,' Geophysical suppl., vol. II, p. 33.

$$\sum_{s'} \mathrm{E}_{s'} \left\{ \rho^{s/2} \left(e^{\iota s\theta} - e^{-\iota s\theta}\right) - \frac{4s'\iota}{\pi} \sum_{n'} \frac{1}{s'^2 - n'^2} \left(e^{\iota n\theta} + e^{-\iota n\theta}\right) \rho^{n/2} \sum_{\nu} \mathrm{A}_\nu^n(s)\, \mathrm{X}_\nu^n \right\} = 0, \tag{15A}$$

for $0 < \theta < \alpha$ and $0 \leqslant \rho \leqslant 1$.

From this the integral corresponding to (18) may be compiled.

The forms of (15) and (15A) are very similar, but it should be noted that there is one very important difference. In (15) $s$, $n$ are integers, while in (15A) $s$, $n$ being $s'\pi/\alpha$, $n'\pi/\alpha$ with $s'$, $n'$ integers, are not in general integers. Hence while $\mathrm{X}_\nu^n$ is an integral function of $\rho$ whatever $n$ may be, the factor $\rho^{n/2}$ has no longer an exponent which is half an integer. It at once becomes evident that the previous process of determining the coefficients E in the velocity condition by equating coefficients of equal powers of $\rho$ becomes inapplicable.

The analogue of (18) is

$$\begin{aligned} \zeta = \sum_{s'} \mathrm{E}_s \Bigg[ & \frac{\rho^{s/2} e^{\iota s\theta}}{\kappa^2 - 4\omega s/\sigma - 2s} - \frac{\rho^{s/2} e^{-\iota s\theta}}{\kappa^2 + 4\omega s/\sigma - 2s} \\ & - \frac{4s'i}{\pi} \sum_{n'} \frac{1}{s'^2 - n'^2} \sum_{\nu} \left\{ \frac{\rho^{n/2} \mathrm{A}_\nu^n(s)\, \mathrm{X}_\nu^n\, e^{\iota n\theta}}{\kappa^2 - 4\omega n/\sigma - 2n - 4\nu(n + \nu + 1)} \right. \\ & \left. + \frac{\rho^{n/2} \mathrm{A}_\nu^n(s)\, \mathrm{X}_\nu^n\, e^{-\iota n\theta}}{\kappa^2 + 4\omega n/\sigma - 2n - 4\nu(n + \nu + 1)} \right\} \Bigg]. \end{aligned} \tag{18A}$$

To form the velocity component $\Theta$ we operate with

$$\frac{2\rho}{f} \frac{\partial \zeta}{\partial \rho} - i \frac{\partial \zeta}{\partial \theta}.$$

Now $\rho \dfrac{\partial \zeta}{\partial \rho}$ and $\dfrac{\partial \zeta}{\theta}$ can each be expanded in a series of Darboux polynomials by the theorem (10). Since the terms of $\zeta$ in $\rho$ are explicit, the coefficients of the Darboux expansions can be completely determined for any given suffix $s$ in the polynomials. This quantity is at our disposal and may be conveniently taken as zero. After this process we should have $\Theta$ expressed as a series of terms $\mathrm{X}_n^0$, with coefficients involving $\theta$ and E. On putting $\theta = 0$, $\alpha$ and equating to zero the complete coefficient of each polynomial, the necessary equations of condition corresponding to (20) may be obtained, and the problem solved. The process is undoubtedly longer than that of the case just worked out, but the method seems to be successful.

### *Semi-circular Basin of Uniform Depth.*

§ 9. We next proceed to outline the application of the present method to the case of a semi-circular basin of *uniform* depth. Taking $h$ to be constant in equation (1) and including also the term corresponding to the tide-producing potential, we have

$$\left.\begin{aligned} \mathrm{R} &= \frac{g}{\sigma^2-4\omega^2}\left(\frac{\partial}{\partial r}-\frac{2\iota\omega}{\sigma r}\frac{\partial}{\partial\theta}\right)(\zeta-\bar{\zeta}) \\ \Theta &= \frac{\iota g}{\sigma^2-4\omega^2}\left(\frac{2\omega}{\sigma}\frac{\partial}{\partial r}-\frac{\iota}{r}\frac{\partial}{\partial\theta}\right)(\zeta-\bar{\zeta}) \\ -\zeta/h &= \frac{\partial(r\mathrm{R})}{r\partial r}+\frac{\partial\Theta}{r\partial\theta} \end{aligned}\right\} . \qquad (23)$$

It is convenient to change the variable $r$ to $\rho = r/a$.* The equations then become

$$\left.\begin{aligned} \mathrm{R} &\propto \left(\frac{\partial}{\partial\rho}-\frac{2\iota\omega}{\sigma\rho}\frac{\partial}{\partial\theta}\right)\zeta' \\ \Theta &\propto \left(\frac{2\omega}{\sigma}\frac{\partial}{\partial\rho}-\frac{\iota}{\rho}\frac{\partial}{\partial\theta}\right)\zeta' \\ (\nabla^2+\kappa^2)\,\zeta &= \nabla^2\bar{\zeta} \end{aligned}\right\}, \qquad (24)$$

where

$$\nabla^2 \equiv \frac{1}{\rho}\frac{\partial}{\partial\rho}\,\rho\,\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial^2}{\partial\theta^2},$$

$$\zeta' = \zeta-\bar{\zeta},$$

and

$$\kappa^2 = (\sigma^2-4\omega^2)\,a^2/gh.$$

The tide-producing potential $\bar{\zeta}$ takes the form

$$\mathrm{A}\rho e^{\iota\theta}+\mathrm{B}\rho e^{-\iota\theta},$$

and hence

$$\nabla^2\bar{\zeta} = 0.$$

The problem is now to solve the equation

$$(\nabla^2+\kappa^2)\,\zeta = 0, \qquad (25)$$

with the added conditions that $\mathrm{R} = 0$ at $\rho = 1$, and $\Theta = 0$ at $\theta = 0, \pi$.

§ 10. We now form the null-function in the same manner as before. Over the range $0 < \theta < \pi$, we have

$$e^{\iota s\theta}-e^{-\iota s\theta}-\frac{4s\iota}{\pi}\sum_n\frac{1}{s^2-n^2}\left(e^{\iota n\theta}+e^{-\iota n\theta}\right) = 0, \qquad (26)$$

$s$, $n$ being integral and $s-n$ odd.

---

* This is to be distinguished from the previous use of $\rho$.

The coefficient unity of each exponent can be expanded in a Dini series

$$1 = \sum_m b_m^s \mathrm{J}_s(\kappa_{sm}\rho) \tag{27}$$

where $\kappa_{sm}$ satisfies the equation

$$\mathrm{J}_s'(\kappa_{sm}) + \frac{2\omega}{\sigma}\frac{s}{\kappa_{sm}}\mathrm{J}_s(\kappa_{sm}) = 0. \tag{28}$$

If the exponent is negative as in $e^{-is\theta}$, the equation determining the root $\kappa_{-sm}$ is

$$\mathrm{J}_s'(\kappa_{-sm}) - \frac{2\omega}{\sigma}\frac{s}{\kappa_{-sm}}\mathrm{J}_s(\kappa_{-sm}) = 0. \tag{28'}$$

Using the standard notation of Watson* we have $\mathrm{H} + \nu = (1 + 2\omega/\sigma)s$ in the case of (28) but $\mathrm{H} + \nu = (1 - 2\omega/\sigma)s$ in the case of (28′).

Hence, $\mathrm{H} + \nu$ may be positive, zero or negative. We shall omit the case $\sigma/2\omega = 1$ as it requires special treatment throughout. When $\mathrm{H} + \nu$ is negative, terms of the form $\mathrm{I}_s(\kappa_{s0}\rho)$ will appear. Provided that $s + \frac{1}{2} \geqslant 0$ ($s$ being taken as the suffix of the J and therefore always satisfying this condition in the present problem) we have the expansions:

(*a*) arising from (28) or (28′) when $\mathrm{H} + \nu$ is positive,

$$1 = \sum_m b_m^s \mathrm{J}_s(\kappa_{sm}\rho),$$

where

$$b_m^s = \frac{2\kappa_{sm}^2 \int_0^1 t\,\mathrm{J}_s(\kappa_{sm}t)\,dt}{(\kappa_{sm}^2 - s^2)\,\mathrm{J}_s^2(\kappa_{sm}) + \kappa_{sm}^2 \mathrm{J'}_s^2(\kappa_{sm})}; \tag{29}$$

and (*b*) when $\mathrm{H} + \nu$ is negative,

$$1 = b_0^s \mathrm{I}_s(\kappa_{s0}\rho) + \sum_{m=1}^{\infty} b_m^s \mathrm{J}_s(\kappa_{sm}\rho),$$

where

$$b_0^s = \frac{2\kappa_{s0}^2 \int_0^1 t\,\mathrm{I}_s(\kappa_{s0}t)\,dt}{(\kappa_{s0}^2 - s^2)\,\mathrm{I}_s^2(\kappa_{s0}) - \kappa_{s0}^2 \mathrm{I'}_s^2(\kappa_{s0})}, \tag{30}$$

and $b_m^s$, $m \neq 0$, is obtained as in (29).

We shall follow Watson in writing both cases as

$$1 = \mathrm{B}_0^s(\rho) + \sum_{m=1}^{\infty} b_m^s \mathrm{J}_s(\kappa_{sm}\rho), \tag{31}$$

where $\mathrm{B}_0^s(\rho)$ is zero for (*a*) and $b_0^s \mathrm{I}_s(\kappa_{s0}\rho)$ for (*b*).

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[*] 'Bessel Functions,' p. 597.

We have, therefore, the null-function in the form

$$\begin{aligned}\sum_s \mathrm{E}_s \Big[ & e^{\iota s\theta}\Big\{\mathrm{B}_0^s(\rho) + \sum_m b_m^s \mathrm{J}_s(\kappa_{sm}\rho)\Big\} \\ & - e^{-\iota s\theta}\Big\{\mathrm{B}_0^{-s}(\rho) + \sum_m b_m^{-s} \mathrm{J}_s(\kappa_{-sm}\rho)\Big\} \\ & - \iota\,.\,\frac{4s}{\pi}\sum_n \frac{1}{s^2-n^2} e^{\iota n\theta}\Big\{\mathrm{B}_0^n(\rho) + \sum_m b_m^n \mathrm{J}_n(\kappa_{nm}\rho)\Big\} \\ & - \iota\,.\,\frac{4s}{\pi}\sum_n \frac{1}{s^2-n^2} e^{-\iota n\theta}\Big\{\mathrm{B}_0^{-n}(\rho) + \sum_m b_m^{-n} \mathrm{J}_n(\kappa_{-nm}\rho)\Big\}\Big]. \qquad (32)\end{aligned}$$

This vanishes identically in the range $0 < \rho < 1$, $0 < \theta < \pi$.

Now consider the solution

$$\begin{aligned}\zeta = \sum_s \mathrm{E}_s \Big[ & e^{\iota s\theta}\Big\{\mathrm{B}_0^s(\rho) \div (\kappa^2 + \kappa_{s0}^2) + \sum_m b_m^s \mathrm{J}_s(\kappa_{sm}\rho) \div (\kappa^2 - \kappa_{sm}^2)\Big\} \\ & - e^{-\iota s\theta}\Big\{\mathrm{B}_0^s(\rho) \div (\kappa^2 + \kappa_{-s0}^2) + \sum_m b_m^{-s} \mathrm{J}_s(\kappa_{-sm}\rho) \div (\kappa^2 - \kappa_{-sm}^2)\Big\} \\ & - \frac{4\iota s}{\pi}\sum \frac{1}{s^2-n^2} e^{\iota n\theta}\Big\{\mathrm{B}_0^n(\rho) \div (\kappa^2 + \kappa_{n0}^2) + \sum_m b_m^n \mathrm{J}_n(\kappa_{nm}\rho) \div (\kappa^2 - \kappa_{-nm}^2)\Big\} \\ & - \frac{4\iota s}{\pi}\sum \frac{1}{s^2-n^2} e^{-\iota n\theta}\Big\{\mathrm{B}_0^{-n}(\rho) \div (\kappa^2 + \kappa_{-n0}^2) \\ & \qquad + \sum_m b_m^{-n} \mathrm{J}_n(\kappa_{-nm}\rho) \div (\kappa^2 - \kappa_{-nm}^2)\Big\}\Big]. \qquad (33)\end{aligned}$$

If we substitute (33) in $(\Delta^2 + \kappa^2)\zeta$, we derive expression (32), which is identically zero within the basin. Hence (33) satisfies the third equation of (24) in the case where $\bar{\zeta} = 0$.

Further, by (28) and (28′), each term of (33) separately makes $\mathrm{R} = 0$ when $\rho = 1$. The solution (33) therefore satisfies one boundary condition and contains an infinite number of arbitrary factors $\mathrm{E}_s$ which may be suitably determined to satisfy the remaining boundary condition.

As a practical point it should be noticed that the solutions of (28) and (28′) can only be obtained when $\sigma/2\omega$ is known. This almost precludes the possibility of determining the values of $\sigma$ for the free oscillations except by long and laborious approximation. For any given value of $\sigma$, however, these equations can be solved and the corresponding critical value of $h$, which only appears in $\kappa^2$, may be determined.

When $\bar{\zeta}$ is not zero, we include in (3) an additional solution of (25), namely,

$CJ_1(\kappa\rho)e^{\iota\theta} + DJ_1(\kappa\rho)e^{-\iota\theta}$. These terms do not of themselves satisfy the first equation (24) at the boundary. But we may take*

$$\begin{aligned}\zeta' = {} & e^{\iota\theta}\{CJ_1(\kappa\rho) - A\rho\} \\ & + e^{-\iota\theta}\{DJ_1(\kappa\rho) - B\rho\}.\end{aligned}$$

The contribution of these terms to the value of R is zero at $\rho = 1$ if

$$C = A(1 + 2\omega/\sigma)/\{\kappa J_1'(\kappa) + 2\omega/\sigma\, J_1(\kappa)\}$$

and

$$D = B(1 - 2\omega/\sigma)/\{\kappa J_1'(\kappa) - 2\omega/\sigma J_1\kappa\}.$$

The value of $\zeta$ given by (33) and those additional terms makes $R = 0$ at $\rho = 1$ for the assumed value of $\bar{\zeta}$.

§ 11. We next turn to the condition that $\Theta = 0$ for $\theta = 0, \pi$. Using the operator $\frac{2\omega}{\sigma}\frac{\partial}{\partial\rho} - \frac{\iota}{\rho}\frac{\partial}{\partial\theta}$ upon $\zeta - \bar{\zeta}$, together with the known relations

$$2J_p'(\kappa\rho) = J_{p-1}(\kappa\rho) - J_{p+1}(\kappa\rho),$$

and

$$\frac{2p}{\rho}J_p(\kappa\rho) = J_{p-1}(\kappa\rho) - J_{p+1}(\kappa\rho),$$

and putting $\theta = 0, \pi$, we have as a result a series of terms each involving $\rho$ within a Bessel function. The Bessel functions have a complete series of integral suffixes but there is a variety of arguments $\kappa_{mn}\rho$. These must be reduced to a common form as may be done by use of the relation

$$J_n(\kappa\rho) = \sum_s b_{2s} J_{n+2s}(\rho),$$

where

$$\begin{aligned}b_{2s} = (-1)^s(n+2s)!\Big\{ & \frac{\kappa^{n+2s}}{s!\,\overline{n+s}!} - \frac{1}{n+2s-1}\cdot\frac{\kappa^{n+2s-2}}{\overline{s-1}!\,\overline{n+s-1}!} \\ & + \frac{1}{(n+2s-1)(n+2s-2)}\cdot\frac{\kappa^{n+2s-4}}{2!\,\overline{s-2}!\,\overline{n+s-2}!}\cdots\Big\}.\end{aligned}$$

It is now possible to form equations corresponding to (21) by equating to zero the collected coefficients of $J_0(\rho)$, $J_1(\rho)$, $J_2(\rho)$, ...

From this point, the solution of the problem follows the same lines as the last.

It will be seen that the present process involves the solution of several sets of transcendental equations. First there are those of (28) and (28′), and four or five roots of each would be required corresponding to each value of *s*. Then there would be the final determinantal equation which would have a form similar to the eliminant of (21). On the other hand, Proudman's method requires only the solution of one determinantal equation. From the practical point of view, therefore, the latter method has the advantage. The process of this paper is, however, worth recording as giving an alternative and also as showing that the problem may be included in the list of those soluble by use of the null-function method.

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* As before $\bar{\zeta} = Are^{\iota\theta/s} + Bre^{-\iota\theta/s}$.

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## *The Formula for the Optical Rotatory Dispersion of Quartz.*

By T. Bradshaw and Prof. G. H. Livens, University College, Cardiff.

(Communicated by Prof. T. M. Lowry, F.R.S.—Received September 27, 1928.)

The optical rotation of quartz has been measured over a large band of wave-lengths. We have Gumlich's* original work over the range from $\lambda = 2 \cdot 140\ \mu$ to $\lambda = 0 \cdot 21935\ \mu$, repeated and extended into the ultra-violet by Soret and Sarasin and Guye. More recently a series of accurate measurements covering the same range was published by Lowry,† and then Duclaux and Jeantet‡ gave a series of results for a range in the ultra-violet from $\lambda = 0 \cdot 30876\ \mu$ to $\lambda = 0 \cdot 185398\ \mu$. Finally, Lowry and Coode-Adams,§ having improved the accuracy of their original method, succeeded in obtaining a very accurate set of readings extending from $\lambda = 2 \cdot 5170\ \mu$ in the infra-red to $\lambda = 0 \cdot 2280\ \mu$ in the ultra-violet, reaching thus just up to the region measured by Duclaux and Jeantet.

Various attempts have been made to fit these results into a formula. Gumlich found it possible to represent his results by a formula of the type

$$\omega = \alpha_1/\lambda^2 + \alpha_2/\lambda^4 + \alpha_3/\lambda^6 + \alpha_4/\lambda^8 + \alpha_5/\lambda^{10},$$

but Kettler had almost equal success with the simpler form

$$\omega = (\lambda^2 - \alpha)/\beta.$$

These two formulæ, although representing the results obtained over the limited range of the spectrum, appear however to have little or no theoretical significance. The first attempt at a theoretical formula was made by Drude in his 'Optics,' where he proposed the form

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* 'Wied. Ann.,' vol. 64, p. 349 (1898).

† 'Phil. Trans.,' A, vol. 212, p. 261 (1912).

‡ 'J. Physique,' vol. 7, p. 200 (1926).

§ 'Phil. Trans.,' A, vol. 226, p. 391 (1927).

$$\omega = A/(\lambda^2 - \lambda_1^2) + B/\lambda^2$$

wherein $\lambda_1^2 = 0\cdot010627$ corresponds to the wave-length (in microns) of the ultra-violet absorption band obtained from refraction data. This formula fitted quite satisfactorily all the results obtained previously to its introduction, but Lowry found that it was not quite accurate enough to include his first series of extended data and he proposed the modified form

$$\omega = A_1/(\lambda^2 - \lambda_1^2) + A_2/(\lambda^2 - \lambda_2^2) + A_3/\lambda^2$$

with

$$\lambda_1^2 = 0\cdot010627, \qquad \lambda_2^2 = 78\cdot22,$$

the latter value corresponding to an infra-red absorption band. His later and still more accurate readings however required still further modification and his final formula is

$$\omega = A_1/(\lambda^2 - \lambda_1^2) + A_2/(\lambda^2 - \lambda_2^2) - A_3$$

where

$$\lambda_1^2 = 0\cdot0127493, \qquad \lambda_2^2 = 0\cdot000974,$$

so that the second band is now right down in the extreme ultra-violet, and the effect of the infra-red band is replaced by a constant.

Neither of these latter formulæ however, represent the results obtained by Duclaux and Jeantet, at least not to within the degree of accuracy claimed for them by their authors,* and it seems as though still further modification is necessary. And, on the face of it, the constant term in Lowry's last formula is most improbable, except as a provisional result, because it is impossible to reconcile it with any theory of these effects.

So far, however, all attempts made to obtain a formula have been based on the assumption that this formula must be more or less of the type suggested by Drude. Certain theoretical considerations developed in detail by one of the present writers† tend, however, to show that the formula must be somewhat more complex. In the case of a medium with, say, three absorption bands at wave-lengths $\lambda_1$, $\lambda_2$, $\lambda_3$—one at least of which is chirally active—it should in fact take the form

$$\omega = \sum_{r=1}^{3} \left\{ \frac{A_r}{\lambda^2 - \lambda_r^2} + \frac{B_r}{(\lambda^2 - \lambda_r^2)^2} \right\},$$

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* That their results are correct to within 0·2° per millimetre.

† 'Phil. Mag.,' vol. 27, p. 994 (1914). The same formula is given by Born in his article "Atomtheorie des festen Zustandes," in the 'Encyclopädie der Mathematischen Wissenschaften' (Bd. V, 3, p. 621) published in 1923. In his book 'Dynamik der Kristallgitter' (Leipzig, 1915), a somewhat different formula is given.

and it has occurred to us to try whether such a formula is capable of adjustment to include the whole set of readings now available. After a number of trials it was found that with

$$\lambda_1^2 = 0{\cdot}01274912, \quad \lambda_2^2 = 0{\cdot}01208000, \quad \lambda_3^2 = 80,$$

the values of the six constants $A_r$, $B_r$ ($r = 1, 2, 3$) could be so chosen that the discrepancies between the observed and calculated values of $\omega$ are all practically within the limits of experimental error. At least the errors are generally no greater than those obtained by Lowry and Coode-Adams with their formula; and whereas their formula does not agree with the experimental results of Duclaux and Jeantet, our formula gives results which differ from those experimental ones by amounts in every case less than the estimated possible errors of observation. Further we find that our formula provides an explanation of the practically constant effect of the infra-red band, as the two terms corresponding to that band in our formula do, in fact, give a practically constant effect throughout the whole range.

In the following tables a comparison of the two formulæ, our own and Lowry's latest and most accurate, is made. Lowry's formula is

$$\omega = \frac{9{\cdot}5639}{\lambda^2 - \lambda_1^2} - \frac{2{\cdot}3113}{\lambda^2 - \lambda_2^2} - 0{\cdot}1905,$$

wherein

$$\lambda_1^2 = 0{\cdot}0127493, \quad \lambda_2^2 = 0{\cdot}000974$$

and is estimated to be accurate to within 0·002° per millimetre over the whole range and to within 0·001 over the more accurate portions.

Our own formula is

$$\omega = \frac{845{\cdot}694}{\lambda^2 - \lambda_1^2} - \frac{0{\cdot}40235}{(\lambda^2 - \lambda_1^2)^2} - \frac{838{\cdot}4320}{\lambda^2 - \lambda_2^2} - \frac{0{\cdot}1331233}{(\lambda^2 - \lambda_2^2)^2} + \frac{43{\cdot}05794}{\lambda^2 - \lambda_3^2} + \frac{2119{\cdot}117}{(\lambda^2 - \lambda_3^2)^2}.$$

In both formulæ and in the tables all wave-lengths are in microns and the rotations in degrees per millimetre.

It may be noticed that in our formula the influence of the infra-red band is retained, and instead of introducing a new band in the extreme ultra-violet, we have only found it necessary to split the old single band into a close doublet.

From the tables it is clear that our new formula is generally more satisfactory than anything that has yet been proposed—as, of course, probably the greater number of adjustable constants might lead one to expect—and it has the advantage of a more satisfactory theoretical basis. There are indications, however, that it may still be possible to improve further on it, for the differences in the visible part of the spectrum, where the greatest accuracy is to be expected, still show a certain amount of regularity. And the ordinary refractive dispersion formula may possibly indicate the directions in which help is to be sought. By using the wave-lengths of the Lowry rotatory dispersion formula Coode-Adams finds that it is possible to fit the refractive index formula with very great accuracy, and this conclusion is advanced in support of the general validity of the original formula. By using the wave-lengths indicated by our rotation formula we find that equally great accuracy is obtainable in the visible and ultra-violet regions, but that to secure agreement in the infra-red region, an additional wave-length in the extreme infra-red region is necessary. This new wave-length can have very little influence on the rotation formula—in the region under consideration—but it might just possibly produce sufficient effect to enable greater accuracy to be secured with the formula. As, however, all the differences are within the limits of experimental error, it is doubtful whether it is worth while pushing the calculations any further at present.

Rotatory Power of Quartz in the Infra-red Region of Spectrum.

| Wave-length, $10^{-8}$ cm. | Observed rotation per millimetre. | Calculated rotation per millimetre. | | Difference. | |
|---|---|---|---|---|---|
| | | Lowry. | Livens. | Lowry. | Livens. |
| 25170 | 0·906 | 0·957 | 0·955 | −0·051 | −0·049 |
| 23900 | 1·087 | 1·082 | 1·079 | +0·005 | +0·008 |
| 22200 | 1·269 | 1·282 | 1·281 | −0·013 | −0·012 |
| 21050 | 1·450 | 1·452 | 1·446 | −0·002 | +0·004 |
| 20000 | 1·631 | 1·630 | 1·623 | +0·001 | +0·008 |
| 19000 | 1·812 | 1·826 | 1·820 | −0·014 | −0·008 |
| 19650 | 1·718 | 1·696 | 1·689 | +0·022 | +0·029 |
| 16640 | 2·443 | 2·443 | 2·436 | +0·000 | +0·007 |
| 16070 | 2·624 | 2·635 | 2·627 | −0·011 | −0·003 |
| 15590 | 2·806 | 2·814 | 2·805 | −0·008 | +0·001 |
| 15170 | 2·987 | 2·983 | 2·975 | +0·004 | +0·012 |
| 14330 | 3·350 | 3·370 | 3·361 | −0·020 | −0·011 |
| 13420 | 3·894 | 3·875 | 3·865 | +0·019 | +0·029 |

Rotatory Power of Quartz in the Red Region of the Spectrum.

| Wave-length, $10^{-8}$ cm. | Observed rotation per millimetre. | Calculated rotation per millimetre. |  | Difference. |  |
|---|---|---|---|---|---|
|  |  | Lowry. | Livens. | Lowry. | Livens. |
| 7741·2 | 12·219 | 12·252 | 12·249 | −0·033 | −0·030 |
| 7641·4 | 12·578 | 12·589 | 12·585 | −0·011 | −0·007 |
| 7443·7 | 13·297 | 13·296 | 13·295 | +0·001 | +0·002 |
| 7172·2 | 14·376 | 14·371 | 14·371 | +0·005 | +0·005 |
| 6930·3 | 15·454 | 15·442 | 15·440 | +0·012 | +0·014 |
| 6854·2 | 15·814 | 15·804 | 15·803 | +0·010 | +0·011 |
| 5821·7 | 22·285 | 22·293 | 22·290 | 0·008 | −0·005 |
| 5652·0 | 23·721 | 23·735 | 23·735 | −0·014 | −0·014 |
| 5392·9 | 26·237 | 26·228 | 26·227 | +0·009 | +0·010 |

Rotatory Power of Quartz in the Visible Region of Spectrum.

| Wave-length, $10^{-8}$ cm. | Observed rotation per millimetre. | Calculated rotation per millimetre. |  | Difference. |  |
|---|---|---|---|---|---|
|  |  | Lowry. | Livens. | Lowry. | Livens. |
| 6708·846 | 16·5359 | 16·5367 | 16·535 | −0·0008 | +0·001 |
| 6438·470 | 18·0243 | 18·0239 | 18·023 | +0·0004 | +0·001 |
| 6362·345 | 18·4797 | 18·4808 | 18·479 | −0·0011 | +0·001 |
| 5895·932 | 21·7010 | 21·7019 | 21·701 | −0·0009 | ±0·000 |
| 5889·965 | 21·7492 | 21·7488 | 21·748 | +0·0004 | +0·001 |
| 5790·659 | 22·5465 | 22·5457 | 22·546 | +0·0008 | ±0·000 |
| 5782·159 | 22·6170 | 22·6160 | 22·616 | +0·0010 | +0·001 |
| 5769·589 | 22·7211 | 22·7206 | 22·720 | +0·0005 | +0·001 |
| 5700·248 | 23·3115 | 23·3108 | 23·312 | +0·0007 | ±0·000 |
| 5471·551 | 25·4328 | 25·4307 | 25·432 | +0·0021 | +0·001 |
| 5465·489 | 25·4921 | 25·4908 | 25·492 | +0·0013 | ±0·000 |
| 5460·742 | 25·5384 | 25·5381 | 25·539 | +0·0003 | −0·001 |
| 5350·65 | 26·6725 | 26·6716 | 26·673 | +0·0009 | ±0·000 |
| 5218·202 | 28·1375 | 28·1393 | 28·140 | −0·0018 | −0·002 |
| 5209·081 | 28·2451 | 28·2446 | 28·246 | +0·0005 | −0·001 |
| 5153·251 | 28·9049 | 28·9042 | 28·906 | +0·0007 | −0·001 |
| 5105·543 | 29·4861 | 29·4864 | 29·488 | −0·0003 | −0·002 |
| 5085·822 | 29·7323 | 29·7321 | 20·733 | +0·0002 | −0·001 |
| 4810·535 | 33·5168 | 33·5175 | 33·519 | −0·0007 | −0·002 |
| 4799·909 | 33·6769 | 33·6780 | 33·679 | −0·0011 | −0·002 |
| 4722·164 | 34·8885 | 34·8895 | 34·890 | −0·0010 | −0·001 |
| 4680·138 | 35·5721 | 35·5722 | 35·573 | −0·0001 | −0·001 |
| 4678·163 | 35·6057 | 35·6049 | 35·605 | +0·0008 | +0·001 |
| 4358·343 | 41·5506 | 41·5504 | 41·553 | +0·0002 | −0·002 |

### Violet and Ultra-violet Regions of the Spectrum.

| Wave-length, $10^{-8}$ cm. | Observed rotation per millimetre. | Calculated rotation per millimetre. | | Difference. | |
|---|---|---|---|---|---|
| | | Lowry. | Livens. | Lowry. | Livens. |
| 2327·49 | 187·247 | 187·247 | 187·23 | ±0·000 | +0·02 |
| 2327·37 | 187·255 | 187·278 | 187·26 | −0·023 | ±0·00 |
| 2331·29 | 186·378 | 186·396 | 186·37 | −0·019 | +0·01 |
| 2332·88 | 186·062 | 186·059 | 186·06 | +0·003 | ±0·00 |
| 2348·40 | 182·726 | 182·708 | 182·70 | +0·018 | +0·03 |
| 2348·23 | 182·734 | 182·743 | 182·74 | −0·009 | −0·01 |
| 2359·12 | 180·439 | 180·447 | 180·45 | −0·008 | −0·01 |
| 2375·193 | 177·143 | 177·143 | 177·14 | ±0·000 | ±0·00 |
| 2382·039 | 175·759 | 175·766 | 177·76 | −0·007 | ±0·00 |
| 2383·253 | 175·526 | 175·523 | 175·52 | +0·003 | +0·01 |
| 2406·663 | 170·951 | 170·947 | 170·95 | +0·004 | ±0·00 |
| 2457·602 | 160·630 | 160·631 | 160·63 | −0·001 | ±0·00 |
| 2527·44 | 150·126 | 150·116 | 150·13 | +0·010 | ±0·00 |
| 2591·554 | 140·663 | 140·657 | 140·67 | +0·006 | −0·01 |
| 2591·554 | 140·669 | 140·655 | 140·67 | +0·014 | ±0·00 |
| 2611·885 | 137·859 | 137·855 | 137·86 | +0·004 | ±0·00 |
| 2611·885 | 137·863 | 137·853 | 137·86 | +0·010 | ±0·00 |
| 2679·065 | 129·199 | 129·187 | 129·21 | +0·012 | −0·01 |
| 2749·324 | 121·039 | 121·031 | 121·03 | +0·008 | +0·01 |
| 2851·800 | 110·511 | 110·504 | 110·51 | +0·007 | ±0·00 |
| 2966·902 | 100·311 | 100·310 | 100·31 | +0·001 | ±0·00 |
| 3083·745 | 91·394 | 91·397 | 91·40 | −0·003 | −0·01 |
| 3239·449 | 81·317 | 81·319 | 81·317 | −0·002 | ±0·000 |
| 3273·965 | 79·315 | 79·319 | 79·317 | −0·004 | −0·002 |
| 3426·646 | 71·337 | 71·331 | 71·331 | +0·006 | +0·006 |
| 3490·577 | 68·360 | 68·355 | 68·355 | +0·005 | +0·005 |
| 3693·999 | 60·058 | 60·060 | 60·059 | −0·002 | −0·001 |
| 3727·622 | 58·838 | 58·839 | 58·837 | −0·001 | +0·001 |
| 4000·250 | 50·077 | 50·078 | 50·080 | −0·001 | −0·003 |
| 4203·985 | 44·980 | 44·981 | 44·981 | −0·001 | −0·001 |

### Extreme Ultra-violet Period.

| Wave-length, $10^{-8}$ cm. | Observed rotation per millimetre. | Calculated rotation per millimetre. | | Difference. | |
|---|---|---|---|---|---|
| | | Lowry. | Livens. | Lowry. | Livens. |
| 2263·09 | 202·365 | 202·435 | 202·41 | −0·07 | −0·04 |
| 2263·14 | 202·365 | 202·423 | 202·38 | −0·06 | −0·02 |
| 2263·34 | 202·27 | 202·37 | 202·33 | −0·10 | −0·06 |
| 2210·03 | 216·50 | 216·51 | 216·44 | −0·01 | +0·06 |
| 2174·02 | 226·91 | 226·98 | 226·89 | −0·08 | +0·02 |
| 1989·79 | 295·65 | 296·24 | 295·75 | −0·59 | −0·05 |
| 1935·18 | 322·76 | 323·64 | 322·74 | −0·88 | +0·02 |
| 1930·30 | 325·31 | 326·29 | 325·38 | −0·98 | −0·07 |
| 1862·09 | 365·6 | 367·45 | 265·7 | −1·90 | −0·1 |
| 1857·35 | 368·6 | 370·62 | 368·8 | −2·00 | −0·2 |
| 1853·98 | 370·9 | 372·91 | 371·08 | −2·00 | −0·2 |

# *On the Form and Potential Energy of the Isomorphous Crystals, Ruby* ($Al_2O_3$) *and Hæmatite* ($Fe_2O_3$).

By J. Topping, M.Sc., Ph.D., D.I.C., Beit Scientific Research Fellow.

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## § 1. *Introduction.*

1.1. Recently, much work has been done in attempting to explain the observed size and shape of crystals in terms of their interionic forces. To do this, a highly idealised form of the crystal has been postulated in which the ions of the crystal (in accordance with Kossel's theory) are regarded as point-charges, of magnitude equal to the resultant ionic charge and situate at the points of the crystal lattice determined by X-ray analysis. For ions which are surrounded symmetrically by other ions, these points doubtless correspond to the nuclei of the respective atoms, but for unsymmetrically situated ions there is some uncertainty as to the exact position to which to assign the point-charge.*

Moreover, in order that the crystal may be in equilibrium, other repulsive forces, in addition to the electrostatic forces of attraction and repulsion between the ionic point-charges, are assumed to be operative between the various ions. These are termed "intrinsic repulsive" forces, and have been represented by an inverse power law varying with the distance according to the $n$th power, and expressible in the form $\mu_n r^{-n}$. Consequently, in order to determine the equilibrium configuration of the crystal, as given by the minimum value of the potential energy of the crystal, it is necessary to determine (i) the electrostatic potential energy of an infinite array of point-charges, arranged according to the crystal pattern, and (ii) the potential energy due to the intrinsic repulsive forces between the ions.

1.2. A method of finding the electrostatic potential energy of periodic systems of point-charges has been given by Madelung,† who applied his formulæ to give the electrostatic potential energy of a simple cubic crystal—NaCl. Also, a general formula giving the electrostatic potential energy of any space-lattice of point-charges has been developed by Ewald,‡ and therefore, theoretically, the electrostatic potential energy of any crystal can be found. This general formula can be applied readily to simple crystals, that is, crystals for which the positions of all the atoms are known when the dimensions of the unit cell have been determined. Applications to more complex crystals are not so easily made; the structures of such crystals generally involve one or more ratios or parameters which may have any value over wide limits without affecting the symmetry of the crystal.

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* *Cf.* 'Roy. Soc. Proc.,' A, vol. 111, p. 51, § 13 (1926).

† 'Phys. Z.,' vol. 19, p. 524 (1918).

‡ M. Born, 'Atomtheorie des festen Zustandes,' p. 727, 2nd ed. (1923).

The calculation of the electrostatic potential energy of complex crystals involving parameters, and an application to give a theoretical explanation of the measured values of these parameters, was first made by W. L. Bragg and S. Chapman.* They considered the carbonate crystals of the calcite type, whose structures involve two parameters. An extension of this work, together with similar calculations for a possible isomorphous series of nitrates, was made later by S. Chapman, J. Topping and J. Morrall.† In all this work, owing to lack of knowledge concerning the intrinsic repulsive forces, only the electrostatic forces were considered, the configuration of minimum energy being found, by using a virtual displacement of the crystal chosen so as to eliminate, as far as possible, any change in the energy corresponding to the intrinsic repulsive forces. However, more recently the contribution of the intrinsic repulsive forces to the total potential energy has been calculated directly, by making use of the data concerning these repulsive forces given by J. E. Lennard-Jones and B. M. Dent.‡ The values of the total potential energy thus obtained have been used to determine the size of the $NO_3^-$ ionic group in the nitrates,§ and of the $CO_3^{--}$ ionic group in the carbonates.||

1.3. The present work relates to still more complex crystals, namely, the members of the isomorphous group including $Al_2O_3$ (ruby), $Fe_2O_3$ (hæmatite), $Cr_2O_3$ and $Ti_2O_3$. These crystals have been assigned to the holohedral class of the rhombohedral system, and their structures involve three parameters. The value of the rhombohedral angle for each crystal is not fixed by the symmetry, and, in fact, may be treated as one of the parameters.

It is shown that the forces considered in this paper (*cf.* § 1.1) can give a very good account of the observed size and shape of the crystals $Al_2O_3$ and $Fe_2O_3$ (the other two crystals of the series cannot be considered since their structures have not been analysed and measured). But in order that the

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* 'Roy. Soc. Proc.,' A, vol. 106, p. 369 (1924).

† 'Roy. Soc. Proc.,' A, vol. 111, p. 25 (1926).

‡ 'Roy. Soc. Proc.,' A, vol. 112, p. 230 (1926).

§ Topping and Chapman, 'Roy. Soc. Proc.,' A, vol. 113, p. 658 (1927).

|| Lennard-Jones and Dent, 'Roy. Soc. Proc.,' A, vol. 113, p. 673 (1927).

theoretical series of possible configurations of the crystal might include the observed configuration, some change is found to be necessary in the intrinsic repulsive-force data given by J. E. Lennard-Jones and B. M. Dent. Further, these crystals are of particular interest because of the approximately hexagonal close-packed arrangement of the O ions, an arrangement which appears to be of great importance in determining the structures of these crystals, as well as those of BeO, $BeAl_2O_4$, $MgAl_2O_4$ and the silicates.* The results of this paper yield some indication of the reason for the observed distortion from an exact hexagonal close-packed system of the O ions in the crystals $Al_2O_3$ and $Fe_2O_3$. This is discussed more fully in § 8.

### § 2. *The Structures of* $Al_2O_3$ *and* $Fe_2O_3$.

2.1. The structure which has been assigned to the $Al_2O_3$ crystal as a result of X-ray measurements,† may be conveniently pictured as follows. A series of rhombic cells is formed by slightly extending cubic cells along a trigonal axis, so that the angles between edges meeting in this axis is about 85° 42′ instead of 90°. At every cell corner is placed a unit consisting of two Al atoms and three O atoms. The two Al atoms are separated by a distance $2d$ of about 2·74 Å. and lie at equal distances from the cell corner along the trigonal axis which passes through it. The three O atoms surround each cell corner at a distance $b$ of about 1·44 Å., lying in a plane through the corner perpendicular to the trigonal axis. Thus the O atoms lie in the (111) planes and they surround the net-points of an equitriangular network, lying along three alternate members of the set of six radii passing through these net-points. The orientation of these groups is completely reversed in successive planes. The structure projected on a (111) plane is shown in fig. 1.

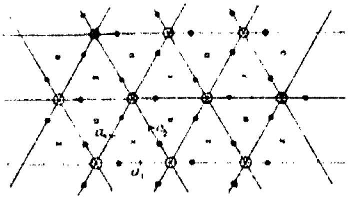

FIG. 1.—The dots represent the $O_3$ groups around the net-points in plane $s = 0$, and the circles represent the Al atoms above and below these net-points. The crosses and squares represent the projections of the net-points in the successive planes $s = 1$ and $s = 2$ respectively.

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* Bragg and West, 'Roy. Soc. Proc.,' A, vol. 114, p. 450 (1927).

† W. L. Bragg, 'Roy. Soc. Proc.,' A, vol. 106, p. 357 (1924); Pauling and Hendricks, 'J. Amer. Chem. Soc.,' vol. 47, p. 781 (1925).

The observed data* for the crystals are indicated below.

| Crystal. | Rhombohedral angle. | Axial ratio $a : 3c$. | $a$ (Davey). | $b$. | $d$. |
|---|---|---|---|---|---|
| | ° ′ | | A. | Å. | Å. |
| $Al_2O_3$ .......... | 85 42⅔ | 1 : 1·3652 | 4·745 | 1·44 ± 0·015 | 1·37 ± 0·03 |
| $Fe_2O_3$ ........ | 85 42 | 1 : 1·3654 | 5·035 | 1·47 ± 0·035 | 1·44 ± 0·05 |

It is clear that the structures involve three parameters which may be chosen in various ways. They may be stated simply as follows :—

(1) The ratio (or some multiple thereof) of the distance $c$ between successive (111) planes to the length of side $a$ of the equitriangular networks in these planes ; that is, a multiple of the axial ratio $a : 3c$.

(2) The ratio (or some multiple thereof) of the O-O distance $b\sqrt{3}$ in the $O_3$ group to the length of side $a$ of the equitriangular network.

(3) The ratio (or some multiple thereof) of the Al-Al distance 2d to the O-O distance in the same $Al_2O_3$ group.

But in the mathematical work it was found convenient to use the following ratios as the parameters : (1) $t = 2\pi a/3\sqrt{3}c$, (2) $\lambda = b/a$, and (3) $d/b$.

Only two particular values of the parameter $d/b$ have been considered, namely, those appropriate to the crystals $Al_2O_3$ and $Fe_2O_3$ respectively. Hence, the main problem discussed is the calculation of the electrostatic potential energy of the $Al_2O_3$ ionic lattice of point-charges involving three parameters, and of the potential energy due to the intrinsic repulsive forces between the various ions. These quantities are calculated for the two particular values of the third parameter and for a series of values of the other two, and the values of these two parameters are then found for the configuration in which the total potential energy of the crystal is a minimum.

## § 3. *The Electrostatic Potential Energy of the* $Al_2O_3$ *Lattice of Point-charges.*

3.1. Owing to the similarity in structure between the carbonates of the calcite type and $Al_2O_3$, the method of finding the electrostatic potential energy of the $Al_2O_3$ ionic lattice follows very closely that used in the case of calcite. It is therefore perhaps only necessary to give a very brief sketch of the method employed and to refer to the former paper† for details.

The electrostatic potential energy $W^{(e)}$ per molecule of the crystal is given by the value of the summation $\frac{1}{2}\Sigma EV$ for the five ions of one $Al_2O_3$ molecule, where V refers to the electrostatic potential at the point-charge E due to all the remaining point-charges. Thus

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* For symbols used in this paper see p. 272.

† S. Chapman, J. Topping and J. Morrall, 'Roy. Soc. Proc.,' A, vol. 111, p. 25 (1926).

$$W^{(e)} = \tfrac{1}{2}\{3eV_{Al+} + 3eV_{Al-} - 3\,.\,2eV_0\},$$

where $V_{Al+}$, $V_{Al-}$ and $V_0$ denote the value of V at the corresponding ions; owing to the symmetry of the structure V has the same value at all ions of the same kind.

Writing the last equation in the form

$$W^{(e)} = \tfrac{1}{2}e\{3V_{Al+} + 3V_{Al-} - 6V_0\} \tag{1}$$

$W^{(e)}/\frac{1}{2}e$ may be interpreted as the potential at a point P due to a composite lattice, $L_P$, formed in an obvious manner.

This composite lattice, $L_P$, consists of groups of point-charges situate at and around the points of equitriangular networks, which are arranged according to the crystal pattern. A complete specification of the charges of this lattice is given in Table I. In writing the positions of the lattice-points it is convenient to make use of the following vectors,

$$\mathbf{r} \equiv s\mathbf{c} + m\mathbf{a}_1 + n\mathbf{a}_2 \tag{2A}$$

$$\mathbf{r}' \equiv \mathbf{r} + \tfrac{1}{3}(\mathbf{a}_1 - \mathbf{a}_3) \tag{2B}$$

$$\mathbf{r}'' \equiv \mathbf{r} + \tfrac{2}{3}(\mathbf{a}_1 - \mathbf{a}_3). \tag{2C}$$

The vectors $\mathbf{r}$, $\mathbf{r}'$, $\mathbf{r}''$ specify the points in fig. 1 which are indicated by circles, crosses and squares respectively; $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are three vectors of equal length **a** and are also indicated in fig. 1. The parameters $s$, $m$, $n$, $l$ take all positive, zero and negative integral values, $s$ referring to different planes and $m$, $n$ referring to the net-points of any one plane. **c** and **d** are vectors parallel to the trigonal axis, **c** being the distance between successive planes of O ions, which are perpendicular to the trigonal axis, and **2d** the distance between the two Al ions of an $Al_2O_3$ group.

Table I.

| Value of $s$. | Positions of lattice-points. | | | Charges at lattice-points. | | | Neutral groups around the lattice-points. | | |
|---|---|---|---|---|---|---|---|---|---|
| | I. | II. | III. | I. | II. | III. | I. | II. | III. |
| $6l$ | $\mathbf{r}$ | $\mathbf{r} \pm \mathbf{d}$ | $\mathbf{r} \pm 2\mathbf{d}$ | $54e$ | $-36e$ | $9e$ | $4G_1$ | $6G_3$ | — |
| $6l+1$ | $\mathbf{r}'$ | $\mathbf{r}' \pm \mathbf{d}$ | $\mathbf{r}' \pm 2\mathbf{d}$ | $54e$ | $-36e$ | $9e$ | $4G_2$ | $6G_4$ | — |
| $6l+2$ | $\mathbf{r}''$ | $\mathbf{r}'' \pm \mathbf{d}$ | $\mathbf{r}'' \pm 2\mathbf{d}$ | $54e$ | $-36e$ | $9e$ | $4G_1$ | $6G_3$ | — |
| $6l+3$ | $\mathbf{r}$ | $\mathbf{r} \pm \mathbf{d}$ | $\mathbf{r} \pm 2\mathbf{d}$ | $54e$ | $-36e$ | $9e$ | $4G_2$ | $6G_4$ | — |
| $6l+4$ | $\mathbf{r}'$ | $\mathbf{r}' \pm \mathbf{d}$ | $\mathbf{r}' \pm 2\mathbf{d}$ | $54e$ | $-36e$ | $9e$ | $4G_1$ | $6G_3$ | — |
| $6l+5$ | $\mathbf{r}''$ | $\mathbf{r}'' \pm \mathbf{d}$ | $\mathbf{r}'' \pm 2\mathbf{d}$ | $54e$ | $-36e$ | $9e$ | $4G_2$ | $6G_4$ | — |

*Four kinds of neutral groups of charges occur which may be denoted by the* letters $G_1$, $G_2$, $G_3$ and $G_4$; they are shown in fig. 2.

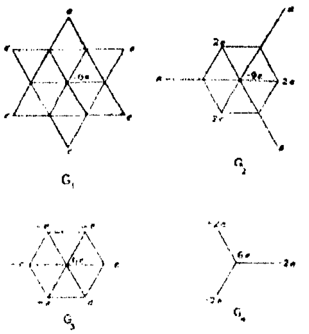

FIG. 2.

To calculate the electrostatic potential at the origin of the system of point-charges specified above in Table I, the following subdivision is made :—

(α) The charges at the lattice-points.

(β) The sets of neutral groups of charges in all the planes $s \neq 0$.

(γ) The sets of neutral groups in the planes corresponding to $s = 0$; these include the $4G_1$ groups in the plane $s = 0$ and the $6G_3$ groups in the planes situated parallel to this at distances **d** above and below.

3.2. Expressions for the potential $V_\alpha$ of the charges at the lattice-points, and the potential $V_\beta$ of the sets of neutral groups in all the planes $s \neq 0$, can be found by using formulæ, originally due to Madelung,* for the electrostatic potential of a linear series and a plane network of point-charges respectively (*cf.* §§ 4 and 5, equations (4) and (7) of the former paper). Some difficulty arose in the evaluation of a series involved in the expression for $V_\beta$, which was relatively slowly convergent for the range of values of the parameters used. But this was avoided by calculating independently the potential of the corresponding network of neutral groups. An algebraic method was used, similar to that given in § 6 of the former paper, and the expression for the potential was found to involve series of the type

$$\sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} \mathrm{R}^{-s} \qquad s = 3, 5, 7,$$

and

$$\sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} (l + \tfrac{2}{3})^n / \mathrm{R}^s \qquad (n, s) = (2, 9), (4, 11) \text{ and } (6, 13),$$

where

$$\mathrm{R}^2 = (l + \tfrac{2}{3})^2 - (l + \tfrac{2}{3})(m + \tfrac{1}{3}) + (m + \tfrac{1}{3})^2.$$

The former are zeta-functions of the second order, which have been dealt with by J. E. Lennard-Jones and A. E. Ingham ;† whilst the second type can be obtained from the first by means of a simple operator successively applied, and an expansion, suitable for computation, can be found.

[*] Madelung, 'Phys. Z.,' vol. 19, p. 524 (1918).

[†] 'Roy. Soc. Proc.,' A, vol. 107, p. 643 (1925).

The potential $V_\gamma$ of the neutral groups in the planes corresponding to $s = 0$ can also be found by methods similar to those used in § 6 of the former paper.

Thus, omitting further details, we may write the potential V of the composite lattice $L_P$ of point-charges as

$$V = -(192e/b) \, . \, F(\lambda, t, d/b), \tag{3}$$

where $F(\lambda, t, d/b)$ is some function of the three parameters. Its value has been calculated for a series of values of the two parameters $\lambda$ and $t$, and for two particular values of the parameter $d/b$. These values are given in Tables IIA and IIB. It might be noted here that the expression (3) for V above does not include the self-potential of the $Al_2O_3$ ionic group which surrounds the origin. This is considered separately later (§ 7).

Table IIA.—Values of $F(\lambda, t, d/b)$. $d/b \doteq 0{\cdot}52 \, . \, \pi/\sqrt{3}$.

| $\lambda/t$. | 2·0. | 2·2. | 2·4. | 2·6. | 2·8. | 3·0. | 3·2. |
|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0·05 | 0·000 00 | 0·000 00 | 0·000 01 | 0·000 01 | 0·000 01 | 0·000 01 | 0·000 01 |
| 0·10 | 0·000 08 | 0·000 13 | 0·000 17 | 0·000 21 | 0·000 24 | 0·000 26 | 0·000 275 |
| 0·15 | 0·000 65 | 0·000 98 | 0·001 295 | 0·001 57 | 0·001 79 | 0·001 96 | 0·002 07 |
| 0·20 | 0·002 83 | 0·004 18 | 0·005 42 | 0·006 48 | 0·007 33 | 0·007 98 | 0·008 405 |
| 0·25 | 0·008 86 | 0·012 64 | 0·016 025 | 0·018 865 | 0·021 115 | 0·022 77 | 0·023 85 |
| 0·28 | 0·015 53 | 0·021 68 | 0·027 085 | 0·031 55 | 0·035 04 | 0·037 55 | 0·039 10 |
| 0·30 | 0·021 885 | 0·030 07 | 0·037 16 | 0·042 94 | 0·047 37 | 0·050 47 | 0·052 26 |
| 0·32 | 0·030 03 | 0·040 58 | 0·049 575 | 0·056 78 | 0·062 18 | 0·065 80 | 0·067 65 |

Table IIB.—Values of $F(\lambda, t, d/b)$. $d/b = 0{\cdot}54 \, . \, \pi/\sqrt{3}$.

| $\lambda/t$. | 2·0. | 2·2. | 2·4. | 2·6. | 2·8. | 3·0. | 3·2. |
|---|---|---|---|---|---|---|---|
| 0·25 | 0·009 775 | 0·013 79 | 0·017 33 | 0·020 25 | 0·022 51 | 0·024 13 | 0·025 115 |
| 0·28 | 0·017 30 | 0·023 82 | 0·029 43 | 0·033 97 | 0·037 41 | 0·039 78 | 0·041 095 |
| 0·30 | 0·024 35 | 0·032 96 | 0·040 25 | 0·046 05 | 0·050 35 | 0·053 19 | 0·054 59 |
| 0·32 | 0·033 35 | 0·044 35 | 0·053 515 | 0·060 65 | 0·065 775 | 0·068 95 | 0·070 175 |

Hence from equations (1) and (3), the electrostatic potential energy per molecule of the crystal is given by

$$W^{(e)} = -(96e^2/b) \, . \, F(\lambda, t, d/b). \tag{4}$$

This may be expressed in heat units per gram-molecule of the crystal as follows:—

$$U^{(e)} = W^{(e)} \, . \, N/J = -(96e^2/b) \, . \, F(\lambda, t, d/b) \, . \, N/J, \tag{4'}$$

where N is the number of molecules per gram-molecule $= 6 \cdot 062 \, . \, 10^{23}$ and J is the mechanical equivalent of heat $= 4 \cdot 184 \, . \, 10^7$ ergs per calorie. $e$ is in electrostatic units and $b$ in centimetres.

### § 4. *The Potential Energy due to the Repulsive Forces.*

The second part of the problem must now be dealt with, namely, that of finding the potential energy due to the intrinsic repulsive forces between the various ions of the crystal.

Considering separately the five ions of an $Al_2O_3$ group (or molecule) surrounding a given net-point of the lattice, the potential energy per molecule of the crystal due to the intrinsic repulsive forces may be expressed in the form

$$W^{(n)} = W_{11}^{(n)} + 2W_{12}^{(n)} + W_{22}^{(n)}, \tag{5}$$

where $W_{11}^{(n)}$ is the potential energy of an Al ion due to all the remaining Al ions; $2W_{12}^{(n)}$ is the potential energy of an $O_3$ ionic group due to all the Al ions, and $2W_{22}^{(n)}$ is the potential energy of an $O_3$ ionic group due to all the remaining O ions. In these quantities the interaction of the ions of the particular $Al_2O_3$ group under consideration is not included; this is considered separately later (*cf.* § 7).

In obtaining expressions for $W_{11}^{(n)}$, $W_{12}^{(n)}$ and $W_{22}^{(n)}$, it is only necessary to take into account a few of the ions nearest to the ion considered, for the total contributions of the remaining ions to these quantities are negligible, owing to the rapid variation of the intrinsic repulsive forces with distance, *i.e.*, according to an inverse 11th power law for neon-like ions such as $O^{--}$ and $Al^{+++}$.

(i) $W_{22}^{(n)}$. Assuming a law of intrinsic repulsive force between O ions of the form $\mu_{22} r^{-n_{22}}$, the expression for $W_{22}^{(n)}$ can be written in the form

$$W_{22}^{(n)} = \tfrac{1}{2} \, . \, 3 \frac{\mu_{22}}{(n_{22} - 1)} \, . \, a^{-(n_{22}-1)} \left[ r_0^{-(n_{22}-1)} + r_1^{-(n_{22}-1)} + r_2^{-(n_{22}-1)} + \ldots \right],$$

where $a \, . \, r_s$ refers to the distances of the O ions in the planes $\pm s$, from an O ion of the $O_3$ group considered in plane $s = 0$.

There is an infinite number of values of each of the distances $ar_s$, but it is only necessary, as explained above, to retain some of their smallest values. Thus, neglecting the unnecessary values, $W_{22}^{(n)}$ can be written in the form

$$W_{22}^{(n)} = \frac{\mu_{22}}{(n_{22} - 1) \, b^{n_{22}-1}} \cdot \phi_{22}^{(n_{22}-1)}, \tag{6}$$

where

$$\phi_{22}^{(n_{22}-1)} = \lambda^{n_{22}-1} \, . \, \Sigma \left( n_0 r_0^{-(n_{22}-1)} + n_1 r_1^{-(n_{22}-1)} + n_2 r_2^{-(n_{22}-1)} \right),$$

and $n_s$ indicates the number of times the distance $ar_s$ occurs. The values of $n_s$ and $r_s$ are indicated in the following scheme.

| $n_0$. | $r_0^2$. | $n_1$. | $r_1^2-4\pi^2/27t^2$. | $n_2$. | $r_2^2-16\pi^2/27t^2$. |
|---|---|---|---|---|---|
| 9 | $1$ | 3 | $\frac{1}{3}+4\lambda^2$ | 9 | $\frac{4}{3}$ |
| 6 | $1+3\lambda^2$ | 3 | $\frac{1}{3}+4\lambda^2-2\lambda$ | 6 | $\frac{4}{3}+3\lambda^2-\lambda$ |
| 6 | $1+3\lambda^2-3\lambda$ | 3 | $\frac{1}{3}+4\lambda^2+2\lambda$ | 6 | $\frac{1}{3}+3\lambda^2+\lambda$ |
| 6 | $1+3\lambda^2+3\lambda$ | 6 | $\frac{1}{3}+\lambda^2$ | 3 | $\frac{1}{3}+3\lambda^2-2\lambda$ |
|  |  | 6 | $\frac{1}{3}+\lambda^2-\lambda$ | 3 | $\frac{4}{3}+3\lambda^2+2\lambda$ |
| 9 | $3$ | 6 | $\frac{1}{3}+\lambda^2+\lambda$ |  |  |
| 6 | $3+3\lambda^2-3\lambda$ |  |  |  |  |
| 6 | $3+3\lambda^2+3\lambda$ | 3 | $\frac{4}{3}+4\lambda^2$ |  |  |
| 3 | $3+3\lambda^2-6\lambda$ | 3 | $\frac{4}{3}+4\lambda^2-4\lambda$ |  |  |
| 3 | $3+3\lambda^2+6\lambda$ | 3 | $\frac{4}{3}+4\lambda^2+4\lambda$ |  |  |
|  |  | 6 | $\frac{4}{3}+\lambda^2$ |  |  |
| 9 | $4$ | 6 | $\frac{4}{3}+\lambda^2-2\lambda$ |  |  |
| 6 | $4+3\lambda^2$ | 6 | $\frac{4}{3}+\lambda^2+2\lambda$ |  |  |
| 6 | $4+3\lambda^2-6\lambda$ |  |  |  |  |
| 6 | $4+3\lambda^2+6\lambda$ |  |  |  |  |

(ii) $W_{12}^{(n)}$. The expression for this part of the energy, assuming a law of intrinsic repulsive force between Al and O ions of the form $\mu_{12}r^{-n_{12}}$, may be written

$$W_{12}^{(n)} = \tfrac{1}{2}\Sigma 2\,\frac{\mu_{12}}{n_{12}-1}\,.\,a^{-(n_{12}-1)}\,r^{-(n_{12}-1)},$$

where $ra$ refers to the distance of the O ions from any Al ion, and the factor 2 is included to account for the two Al ions of the $Al_2O_3$ group.

Further, this may be expressed in the form

$$W_{12}^{(n)} = \frac{\mu_{12}}{(n_{12}-1)\,b^{n_{12}-1}}\cdot\phi_{12}^{(n_{12}-1)}, \tag{7}$$

where

$$\phi_{12}^{(n_{12}-1)} = \lambda^{n_{12}-1}\sum_{s} n_s r_s^{-(n_{12}-1)},$$

and the values of $r_s$ and $n_s$ (the number of times the distance $ar_s$ occurs) are indicated below.

| $n_1$. | $r_1^2-d^2/a^2$. | $n_2$. | $r_2^2-(c-d)^2/a^2$. | $n_3$. | $r_3^2-(2c-d)^2/a^2$. | $n_4$. | $r_4^2-(c+d)^2/a^2$. |
|---|---|---|---|---|---|---|---|
| 3 | $(1-\lambda)^2$ | 3 | $\frac{1}{3}+\lambda^2$ ; $\frac{4}{3}+\lambda^2$ | 3 | $\frac{1}{3}+\lambda^2$ | 3 | $\frac{1}{3}+\lambda^2$ |
| 3 | $(1+\lambda)^2$ | 3 | $\frac{1}{3}+\lambda^2-\lambda$ ; $\frac{4}{3}+\lambda^2-2\lambda$ | 3 | $\frac{1}{3}+\lambda^2-\lambda$ | 3 | $\frac{1}{3}+\lambda^2-\lambda$ |
| 6 | $1-\lambda+\lambda^2$ | 3 | $\frac{1}{3}+\lambda^2-\lambda$ ; $\frac{4}{3}+\lambda^2+2\lambda$ | 3 | $\frac{1}{3}+\lambda^2+\lambda$ | 3 | $\frac{1}{3}+\lambda^2+\lambda$ |
| 6 | $1+\lambda+\lambda^2$ |  |  |  |  |  |  |

(iii) $W_{11}^{(n)}$. An expression similar to (6) and (7) can be found for $W_{11}^{(n)}$, viz.,

$$W_{11}^{(n)} = \frac{\mu_{11}}{(n_{11}-1)\,b^{n_{11}-1}}\cdot\phi_{11}^{(n_{11}-1)}. \tag{8}$$

and it may be shown that $\phi_{11}^{(10)}$ is considerably less than the corresponding values of $\phi_{22}^{(10)}$ and $\phi_{12}^{(10)}$, whilst $\mu_{11}$ also is comparatively very small. For if $\rho^{+}$ be the diameter of an $Al^{+++}$ ion, and $\mu$ and $\rho$ be the force-constant and diameter respectively of neon atoms, the force-constant $\mu_{11}$ for Al ions is given by

$$\mu_{11}/\mu = (\rho^{+}/\rho)^{n_{11}-1}. \tag{8'}$$

Thus, if we assume a probable value of the ratio of the size of the Al ion to that of the neon atom, and use the value of $\mu$ for neon atoms (corresponding to $n_{11} = 11$) given by Lennard-Jones, it is found that $\mu_{11}$ is about 0·01 or 0·02. Consequently, the value of $W_{11}^{(n)}$ is very small compared with $W_{22}^{(n)}$ and $W_{12}^{(n)}$, and has therefore been neglected in these calculations.

Thus equation (5) becomes

$$W^{(n)} = 2W_{12}^{(n)} + W_{22}^{(n)} \tag{5'}$$

and expressions for $W_{12}^{(n)}$ and $W_{22}^{(n)}$ have been found in terms of the force-constants and force-indices $\mu_{12}$, $\mu_{22}$ and $n_{12}$, $n_{22}$; and the three parameters $\lambda$, $t$ and $d/b$.

Further, expressing the energy in heat units (calories) per gram-molecule, equation (5′) becomes

$$U^{(n)} = 2U_{12}^{(n)} + U_{22}^{(n)}, \tag{5''}$$

where

$$U_{lm}^{(n)} = W_{lm}^{(n)} \,.\, N/J = \frac{\mu_{lm}}{(n_{lm}-1)\, b^{n_{lm}-1}} \,.\, \Phi_{lm}^{(n_{lm}-1)} \qquad (l, m = 1, 2),$$

writing

$$\Phi_{lm}^{(n_{lm}-1)} = \phi_{lm}^{(n_{lm}-1)} \,.\, N/J.$$

Here $N = 6{\cdot}062 \,.\, 10^{23}$ and $J = 4{\cdot}184 \,.\, 10^{7}$ ergs per calorie.

Values of the functions $\Phi_{12}^{(10)}$ and $\Phi_{22}^{(10)}$ (since $n_{12} = n_{22} = 11$ for neon-like ions) have been calculated for a series of suitable values of $\lambda$ and $t$, and for two particular values of $d/b$. These values are given in Tables III, IVA and IVB.

## § 5. *The Total Potential Energy.*

The total potential energy of the crystal expressed in heat units per gram-molecule is given by

$$U = U^{(e)} + U^{(n)}, \tag{9}$$

where $U^{(e)}$ and $U^{(n)}$ are defined by equations (4′) and (5″) respectively. The values of $U^{(e)}$ can be found from Tables IIA and IIB, and the values of $U^{(n)}$ can be obtained by using the values of the functions $\Phi_{lm}^{(10)}$ given in Tables III, IVA and IVB.

### Table III.—Values of $\Phi_{22}^{(10)}$.

| $t/\lambda$. | 0·25. | 0·26. | 0·27. | 0·28. | 0·29. | 0·30. | 0·31. | 0·32. |
|---|---|---|---|---|---|---|---|---|
| 2·0 | 0·105 56 . $10^{14}$ | 0·171 84. $10^{14}$ | 0·276 70 . $10^{14}$ | 0·441 14 . $10^{14}$ | 0·069 69 . $10^{15}$ | 0·109 17 . $10^{15}$ | 0·169 59 . $10^{15}$ | 0·261 31 . $10^{15}$ |
| 2·2 | 0·156 67 | 0·249 26 | 0·391 65 | 0·609 15 | 0·093 72 | 0·143 10 | 0·216 85 | 0·326 32 |
| 2·4 | 0·241 92 | 0·378 62 | 0·583 89 | 0·889 00 | 0·133 88 | 0·199 76 | 0·295 70 | 0·434 72 |
| 2·6 | 0·374 60 | 0·580 19 | 0·883 48 | 1·325 48 | 0·196 35 | 0·287 75 | 0·417 96 | 0·602 60 |
| 2·8 | 0·569 32 | 0·876 19 | 1·323 16 | 1·965 17 | 0·287 72 | 0·416 20 | 0·596 07 | 0·846 81 |
| 3·0 | 0·841 12 | 1·289 36 | 1·936 23 | 2·855 39 | 0·414 56 | 0·594 04 | 0·842 12 | 1·183 57 |
| 3·2 | 1·204 54 | 1·841 59 | 2·754 39 | 4·040 59 | 0·582 95 | 0·829 44 | 1·166 92 | 1·627 26 |

### Table IVA.—Values of $\Phi_{12}^{(10)}$. $d/b \doteqdot 0\cdot52 . (\pi/\sqrt{3})$.

| $t/\lambda$. | 0·25. | 0·26. | 0·27. | 0·28. | 0·29. | 0·30. | 0·31. | 0·32. |
|---|---|---|---|---|---|---|---|---|
| 2·0 | 0·025 28 . $10^{15}$ | 0·045 70 . $10^{15}$ | 0·081 73 . $10^{15}$ | 0·144 74 . $10^{15}$ | 0·253 95 . $10^{15}$ | 0·044 17 . $10^{16}$ | 0·076 16 . $10^{16}$ | 0·130 28 . $10^{16}$ |
| 2·2 | 0·050 22 | 0·092 14 | 0·167 21 | 0·300 32 | 0·534 08 | 0·094 08 | 0·164 21 | 0·284 03 |
| 2·4 | 0·088 19 | 0·163 37 | 0·299 15 | 0·541 76 | 0·970 73 | 0·172 14 | 0·302 16 | 0·525 03 |
| 2·6 | 0·139 13 | 0·259 07 | 0·476 49 | 0·865 96 | 1·555 63 | 0·276 28 | 0·485 12 | 0·842 09 |
| 2·8 | 0·200 57 | 0·374 05 | 0·688 41 | 1·250 71 | 2·243 66 | 0·397 44 | 0·695 14 | 1·200 18 |
| 3·0 | 0·268 39 | 0·499 89 | 0·917 92 | 1·662 26 | 2·968 78 | 0·522 91 | 0·908 14 | 1·554 56 |
| 3·2 | 0·338 03 | 0·627 46 | 1·147 16 | 2·066 10 | 3·665 80 | 0·640 64 | 1·102 43 | 1·867 17 |

### Table IVB.—Values of $\Phi_{12}^{(10)}$. $d/b = 0\cdot54. (\pi/\sqrt{3})$.

| $t/\lambda$. | 0·25. | 0·26. | 0·27. | 0·28. | 0·29. | 0·30. | 0·31. | 0·32. |
|---|---|---|---|---|---|---|---|---|
| 2·0 | 0·028 26 . $10^{15}$ | 0·051 45 . $10^{15}$ | 0·092 73 . $10^{15}$ | 0·165 49 . $10^{15}$ | 0·292 64 . $10^{15}$ | 0·051 30 . $10^{16}$ | 0·089 11 . $10^{16}$ | 0·153 73 . $10^{16}$ |
| 2·2 | 0·056 13 | 0·103 70 | 0·189 50 | 0·342 72 | 0·613 70 | 0·108 85 | 0·191 27 | 0·333 03 |
| 2·4 | 0·098 20 | 0·183 02 | 0·337 13 | 0·614 10 | 1·106 57 | 0·197 30 | 0·348 10 | 0·607 77 |
| 2·6 | 0·153 95 | 0·288 09 | 0·532 36 | 0·971 83 | 1·753 03 | 0·312 50 | 0·550 51 | 0·958 18 |
| 2·8 | 0·220 15 | 0·412 11 | 0·761 02 | 1·386 75 | 2·493 90 | 0·442 61 | 0·775 10 | 1·338 86 |
| 3·0 | 0·291 94 | 0·545 11 | 1·002 99 | 1·818 93 | 3·251 24 | 0·572 71 | 0·993 88 | 1·698 44 |
| 3·2 | 0·364 21 | 0·676 93 | 1·238 45 | 2·230 51 | 3·954 46 | 0·689 96 | 1·184 22 | 1·998 41 |

Thus the total potential energy of the crystal can be found for any value of $b$ and any values of the force-constants $\mu_{22}$ and $\mu_{12}$. A typical set of results is shown in Table V, which gives the values of $-\mathrm{U}$ for $b = 1 \cdot 45$ Å., with $\mu_{22} = 11 \cdot 0$, $\mu_{12} = 2 \cdot 0$ and $d/b = 0 \cdot 54 \,.\, \pi/\sqrt{3}$ (a combination of values referred to later as II (4) ). The values of $-\mathrm{U}$ are given in terms of large calories as units.

Table V.—Values of the Total Potential Energy—U.

| $\lambda/t$. | 2·0. | 2·2. | 2·4. | 2·6. | 2·8. | 3·0. | 3·2. |
|---|---|---|---|---|---|---|---|
| 0·25 | 208·1 | 291·9 | 362·9 | 417·7 | 455·5 | 476·5 | 481·4 |
| 0·26 | 251·0 | 348·0 | 427·8 | 486·8 | 524·3 | 540·9 | 537·3 |
| 0·27 | 298·8 | 408·6 | 495·3 | 554·8 | 586·8 | 593·0 | 574·8 |
| 0·28 | 350·3 | 471·0 | 559·9 | 612·6 | 630·2 | 616·1 | 573·1 |
| 0·29 | 403·2 | 530·0 | 611·7 | 644·8 | 632·8 | 582·2 | 498·9 |
| 0·30 | 453·1 | 570·2 | 634·4 | 625·5 | 558·4 | 446·2 | 299·7 |
| 0·31 | 492·8 | 594·3 | 600·0 | 511·4 | 348·3 | 135·7 | —107·0 |
| 0·32 | 509·4 | 558·0 | 461·9 | 231·8 | — 92·2 | —463·1 | —847·1 |

## § 6. *Graphical Representation of the Results.*

Having obtained the values of the total potential energy U for a series of values of the parameters $\lambda$ and $t$, and for any particular values of $b$, $d/b$, $\mu_{22}$ and $\mu_{12}$, it is possible to draw on a $(\lambda, t)$ diagram a series of contour curves passing through points for which the value of U is constant. The curves corresponding to the values of U given in Table V are shown in fig. 3; the numbers on each curve indicate the corresponding value of the total energy $-\mathrm{U}$ in large calories per gram-molecule. Similar curves have been obtained for other values of $b$, $d/b$, $\mu_{22}$ and $\mu_{12}$.

Each set of curves defines a limiting-point $\mathrm{P}_m$, which is obtained by finding the point of intersection P of two diameters of each oval; $\mathrm{P}_m$ is the limiting position of the various points P for the different ovals. It is clear that for the values of the parameters $(\lambda_m, t_m)$ corresponding to the point $\mathrm{P}_m$, the value of the total potential energy, $\mathrm{U}_m$ say (being negative), is a minimum, and so $(\lambda_m, t_m)$ define a configuration of the crystal which is in stable equilibrium. And if the values of $b$, $d/b$, $\mu_{22}$ and $\mu_{12}$ were known with certainty, the values of $(\lambda_m, t_m)$ thus obtained should correspond to the actual form of the crystal. However, since there is some uncertainty concerning the values of $\mu_{22}$ and $\mu_{12}$, and some experimental error in the values of $b$ and $d/b$, an attempt is made to obtain values of these quantities which will best explain the observed values of the distance $a$ and the rhombohedral angle $\alpha$ of the crystals. Consequently, curves have been drawn for various values of $b$ and $d/b$, and for different combinations of values of $\mu_{22}$ and $\mu_{12}$, and the values of the minimum potential energy $U_m$ and of the parameters $\lambda_m$ and $t_m$ have been found in each case.

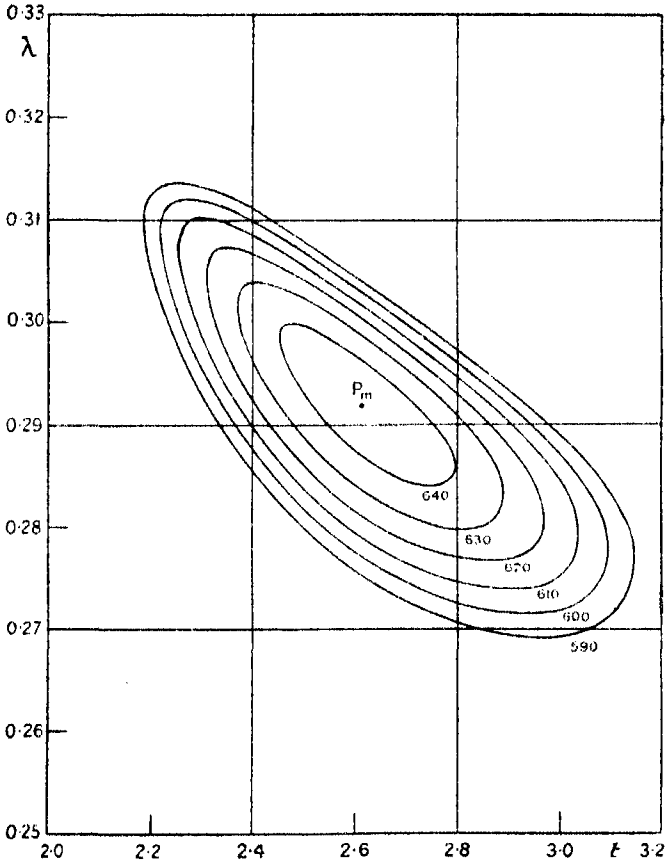

FIG. 3.

It should be noted that this determination of $(\lambda_m, t_m)$ is unaffected by the addition to U of the potential energy of the $Al_2O_3$ group around the origin, which has been neglected both in the calculation of the electrostatic energy and of the energy due to the repulsive forces (*cf.* § 7). For the potential energy of this group is independent of $\lambda$ and $t$, depending only upon the other parameter $d/b$, and, of course, the force-constants $\mu_{12}$ and $\mu_{22}$. Also the real minimum value of the energy will be obtained by the addition to $U_m$, of the potential energy of this group for the appropriate values of $b$, $d/b$, $\mu_{22}$ and $\mu_{12}$. This is considered in detail later.

The values of $\lambda_m$ and $t_m$, obtained as described above, may be plotted on a $(\lambda, t)$ diagram, so that a curve, say, $t_m = \phi(\lambda_m)$, is obtained which has one value of $b$ (a parameter of the curve) corresponding to each point. However, a more convenient graphical representation of the results is obtained by using as co-ordinates $a_m$ and $\alpha_m$, the values of the interatomic distance and the rhombohedral angle respectively in the position of minimum potential energy, which are connected with $\lambda_m$ and $t_m$ by the relations

$$b = \lambda_m a_m \text{ and } \operatorname{cosec}^2 \tfrac{1}{2}\alpha_m = 4\left(\tfrac{1}{3} + 4\pi^2/27t_m^2\right).$$

We thus obtain a curve, $\alpha_m = \psi(a_m)$ say, which also has one value of $b$ corresponding to each point.

The results are collected in fig. 4, where P corresponds to the observed values of $a_m$ and $\alpha_m$ for $Al_2O_3$, viz., $a_m = 4\cdot745$ Å. and $\alpha_m = 85° \ 42\tfrac{2}{3}'$, and Q refers to $Fe_2O_3$, viz., $a_m = 5\cdot035$ Å and $\alpha_m = 85° \ 42'$.

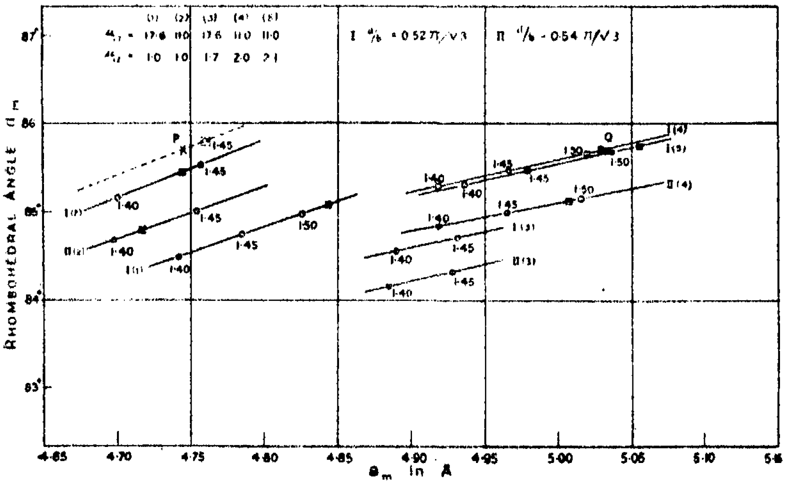

FIG. 4.

The curve marked I(1) corresponds to the values $d/b = 0\cdot52\,\pi/\sqrt{3}$, $\mu_{22} = 17\cdot6$ and $\mu_{12} = 1\cdot0$, and the points corresponding to $b = 1\cdot40$, $1\cdot45$ and $1\cdot50$ Å are indicated. An attempt was then made to change the force-constants so as to obtain a curve nearer to the "observed" point P, and it was found that by changing $\mu_{22}$ from 17·6 to 11·0 the curve, marked I(2), was obtained. The curve, marked II(2), corresponds to I(2) but with the value of the parameter $d/b$ changed to $0\cdot54\,\pi/\sqrt{3}$.

The curve marked II(3) is obtained by using the values $d/b = 0\cdot54\,\pi/\sqrt{3}$, $\mu_{22} = 17\cdot6$ and $\mu_{12} = 1\cdot7$; and the curve marked I(3) is the corresponding curve for the other value of $d/b = 0 \cdot 52\, \pi/\sqrt{3}$. Again, by altering the force-constants to $\mu_{22} = 11 \cdot 0$ and $\mu_{12} = 2 \cdot 0$ the curves, marked I(4) and II(4) respectively, are obtained for the two values of the parameter $d/b$. The further curve I(5) is obtained by using the values $d/b = 0 \cdot 52\, \pi/\sqrt{3}$, $\mu_{22} = 11 \cdot 0$ and $\mu_{12} = 2 \cdot 1$.

### § 7. *The Addition of the Energy due to the remaining* $Al_2O_3$ *Group.*

The electrostatic potential energy $U_0^{(e)}$ of this remaining $Al_2O_3$ group around the origin is simply that of the charges which have been neglected, viz., a $4G_1$ group of charges in the plane $z = 0$, *a* $6G_3$ group in each of the planes $z = \pm d$ and charges $9e$ at $z = \pm 2d$ and $-36e$ at $z = \pm d$. Thus we have

$$U_0^{(e)} = \tfrac{1}{2} \,.\, e^2/b\, [8\sqrt{3} - 72\,(1 + d^2/b^2)^{-\frac{1}{2}} + 9\,(b/d)] \,.\, N/J,$$

$$= -\, 1/b \,.\, 4 \cdot 784\ 42 \,.\, 10^6 \quad \text{for } d/b = 0 \cdot 52\, \pi/\sqrt{3},$$

and

$$-\, 1/b \,.\, 4 \cdot 687\ 68 \,.\, 10^6 \quad \text{for } d/b = 0 \cdot 54\, \pi/\sqrt{3}$$

in calories per gram-molecule with $b$ in Å units.

Further, the energy of this $Al_2O_3$ group due to the intrinsic repulsive forces can easily be found to be

$$U_0^{(n)} = 1/b^{10} \,.\, [\mu_{22}/81 + 6\mu_{12}\,(1 + d^2/b^2)^{-5} + \mu_{11}\,(b/2d)^{10}] \,.\, N/J \,.\, 10^{-9}$$

expressed in calories per gram-molecule, with $b$ in Å units.

The values of $U_0$, that is, $U_0^{(e)} + U_0^{(n)}$, the total energy of the group, are indicated below in Table VI for various values of the three quantities $d/b$, $b$, $\mu_{22}$ and $\mu_{12}$. The notation is the same as in fig. 4 ; for instance, I(2) refers to

$$d/b = 0 \cdot 52 \,.\, \pi/\sqrt{3}, \qquad \mu_{22} = 11 \cdot 0 \quad \text{and} \quad \mu_{12} = 1 \cdot 0.$$

The values of $U_m$, obtained as described in § 6, are also indicated together with the values of the total energy $U_0 + U_m$. The units are large calories per gram-molecule.

Table VI.

| | $b$. | $U_0^{(e)}$. | $U_0^{(n)}$. | $U_0$. | $U_m$. | $U_0+U_m$. |
|---|---|---|---|---|---|---|
| I(2) | 1·40 | 3 417 | 192 | 3 225 | 674 | 3 899 |
| | 1·45 | 3 300 | 136 | 3 164 | 740 | 3 904 |
| | 1·50 | 3 190 | 97 | 3 093 | 805 | 3 898 |
| | 1·55 | 3 087 | 70 | 3 017 | (870) | 3 887 |
| I(4) | 1·40 | 3 417 | 317 | 3 100 | 555 | 3 655 |
| | 1·45 | 3 300 | 224 | 3 076 | 609 | 3 685 |
| | 1·50 | 3 190 | 159 | 3 031 | 663 | 3 694 |
| | 1·55 | 3 087 | 115 | 2 972 | (717) | 3 689 |
| I(5) | 1·40 | 3 417 | 330 | 3 087 | 545 | 3 632 |
| | 1·45 | 3 300 | 232 | 3 068 | 599 | 3 667 |
| | 1·50 | 3 190 | 166 | 3 024 | 654 | 3 678 |
| | 1·55 | 3 087 | 119 | 2 968 | (708) | 3 676 |
| II(4) | 1·40 | 3 348 | 276 | 3 072 | 592 | 3 664 |
| | 1·45 | 3 233 | 194 | 3 039 | 648 | 3 687 |
| | 1·50 | 3 125 | 138 | 2 987 | 704 | 3 691 |
| | 1·55 | 3 024 | 100 | 2 924 | (760) | 3 684 |

### § 8. *Discussion of the Results.*

8.1. We will first consider the curve I (1) in fig. 4. The value of the parameter $d/b$ for this curve is very nearly equal to the observed value for $Al_2O_3$, and the value of $\mu_{22} = 17 \cdot 6$ is the value of the force-constant for O ions given by J. E. Lennard-Jones and B. M. Dent.[*] The value of $\mu_{12}$ for Al and O ions has not been found, but an estimate of its value can be made. It has been indicated in § 4 how an approximate value of $\mu_{11}$ for $Al^{+++}$ ions can be obtained, so that using the relation[†]

$$\mu_{12}^{1/(n-1)} = \tfrac{1}{2}\left(\mu_{11}^{1/(n-1)} + \mu_{22}^{1/(n-1)}\right) \tag{10}$$

and the values of $\mu_{11}$ and $\mu_{22}$, an approximate value of $\mu_{12}$ is found, viz., $\mu_{12} = 1 \cdot 0$.

The curve I (1) corresponds to these values of $d/b$, $\mu_{22}$ and $\mu_{12}$ for $Al_2O_3$, but it does not pass through the point P corresponding to the observed values of $a_m$ and $\alpha_m$ for $Al_2O_3$, which signifies that the above values of $d/b$, $\mu_{22}$ and $\mu_{12}$ which have been used will not give an exact explanation of the observed size and shape of the crystal.

A comparison of the curves I (1) and I (3) gives an indication of how a change in the force-constant $\mu_{12}$ alone (from 1·0 to 1·7) affects the results. The curve undergoes a comparatively large translatory shift almost parallel to the

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[*] 'Roy. Soc. Proc.,' A, vol. 112, p. 230 (1926).

[†] *Cf.* equation (2.05), 'Roy. Soc. Proc.,' A, vol. 109, p. 483 (1925).

$\alpha$-axis, which shows that no probable change in $\mu_{12}$ alone will yield a curve passing through the "observed" point P. For in order to accomplish this, $\mu_{12}$ would have to be reduced to nearly zero, and such a large change is untenable. But the curve I (2) indicates that some change in the force-constant $\mu_{22}$ alone will produce a displacement of the curve so as to make it pass through P. Also the curve II (2) shows that by increasing the value of the parameter $d/b$, the curve is moved further away from P, and hence it might be concluded that an appropriate decrease in this parameter will give a curve passing through P; with $\mu_{22} = 11 \cdot 0$, the value $d/b = 0 \cdot 51 \,.\, \pi/\sqrt{3}$ would seem to be suitable. It is therefore clear that retaining the value $\mu_{12} = 1 \cdot 0$, suitable changes in $\mu_{22}$ and $d/b$ will give a curve passing through P. Also these possible changes may be conveniently chosen so as to obtain a minimum value of the total potential energy $U_0 + U_m$, corresponding to a value of $b$ as near as possible to the observed value. The various possible changes will thereby be much restricted.

The sets of values of the total energy $U_0 + U_m$, some of which are given in Table VI, are of great interest, because they all indicate a definite minimum value of the energy, which would seem to show that the forces treated of in this paper can give a very good account of the equilibrium of the crystals. This fact is of greater interest since it was not possible to obtain definite energy minima for the crystals of sodium nitrate $NaNO_3$ and calcium carbonate $CaCO_3$ (*cf.*, 'Roy. Soc. Proc.,' A, vol. 113, pp. 672-3 (1927)). In fig. 4 the point on each curve corresponding to the minimum value of the total energy $U_0 + U_m$ is indicated by a square.

For the combination of values of $\mu_{22}$, $\mu_{12}$ and $d/b$ indicated by I (1), the values of $U_0 + U_m$ have a minimum value (maximum numerically) for a value of $b$ between $1 \cdot 50$ and $1 \cdot 55$ Å. For the values I (2) the minimum value of the energy occurs for $b = 1 \cdot 44$ Å approximately, which is in excellent agreement with the observed value of $1 \cdot 44$ Å $\pm\, 0 \cdot 015$ for the $Al_2O_3$ crystal. Moreover, the values of $a_m$ and $\alpha_m$ at the point on the curve I (2) corresponding to $b = 1 \cdot 44$ are $4 \cdot 745$ Å and 85° 27′ respectively, which agree very well with the observed values, viz., $4 \cdot 745$ Å and 85° 42⅔′. Of course this agreement will be slightly changed, but not impaired, for a curve passing exactly through P. For instance, the curves I (2) and II (2) indicate that for a value of $d/b$ approximately equal to $0 \cdot 51\, \pi/\sqrt{3}$ a curve will be obtained which passes through the point P, and, further, that the point of "absolute" minimum energy (that is, the minimum value of $U_0 + U_m$) on this curve corresponds to a value of $b = 1 \cdot 45$ Å approximately. And at this point the values of $a_m$ and $\alpha_m$ are about 4·76 Å and 85° 48′ respectively. This probable curve through P is indicated by a dotted line in fig. 4. It is therefore sufficiently clear that we can derive an estimate of the force-constants $\mu_{22}$ and $\mu_{12}$, and of the ratio $d/b$, which will give an accurate account of the observed values of $a_m$, $\alpha_m$ and $b$ for the $Al_2O_3$ crystal. Before doing this we can consider the information obtainable from the curves which correspond more nearly to the crystal $Fe_2O_3$.

8.2. The observed value of the parameter $d/b$ for $Fe_2O_3$ is $1{\cdot}44/1{\cdot}47$ (neglecting probable errors of measurements) which is almost exactly equal to the second value of $d/b$ that has been used, viz., $d/b = 0{\cdot}54 \,.\, \pi/\sqrt{3}$. Also a value of $\mu_{12} = 1{\cdot}7$ for $Fe^{++}$ and $O^{--}$ ions has been found by J. E. Lennard-Jones and B. M. Dent* from calculations on $FeCO_3$, and so this value was used tentatively, although in $Fe_2O_3$ the Fe ion is not doubly, but trebly ionised. The curve II (3) corresponds to the values $d/b = 0{\cdot}54 \,.\, \pi/\sqrt{3}$, $\mu_{22} = 17{\cdot}6$ and $\mu_{12} = 1{\cdot}7$, which thus appear to be inadequate to explain the observed data of $Fe_2O_3$. The curve II (4) is obtained by altering the force-constants to $\mu_{22} = 11{\cdot}0$ and $\mu_{12} = 2{\cdot}0$, which indicates that no probable changes in the force-constants alone would displace the curve sufficiently as to make it pass through the "observed" point Q. However, if the other value of the parameter $d/b$, viz., $0{\cdot}52\,\pi/\sqrt{3}$, be used, keeping $\mu_{22} = 11{\cdot}0$ and $\mu_{12} = 2{\cdot}0$, a curve is obtained which passes almost exactly through the point Q, that is, the curve I (4). The curve I (5) indicates the further alteration effected by changing $\mu_{12}$ from 2·0 to 2·1. This curve also almost passes through Q.

The values of $U_0 + U_m$ corresponding to the curves I (4) and I (5) are given in Table VI, and they indicate "absolute" minima of the energy for values of $b$ equal to 1·51 Å and 1·52 Å approximately. These values are in good agreement with the observed value of $b = 1{\cdot}47$ Å ± 0·035 for $Fe_2O_3$. Also corresponding to these values of $b$ the values of $a_m$ and $\alpha_m$ given by the curves I (4) and I (5) are 5·03 Å, 85° 42′ and 5·055 Å, 85° 45′ respectively, which are in very good accord with the observed values of 5·035 Å and 85° 42′. It is, therefore, clear, as in the case of $Al_2O_3$, that a convenient choice of the values of the force-constants $\mu_{22}$, $\mu_{12}$ and the ratio $d/b$ can be made in order to give an accurate account of the observed quantities involved in the crystal structure, viz., $a_m$, $\alpha_m$ and $b$.

8.3. The combined results for $Al_2O_3$ and $Fe_2O_3$ would therefore seem to indicate that in order to explain the observed crystal data, it is necessary to adopt a value of $\mu_{22}$ different from that given by J. E. Lennard-Jones and B. M. Dent, and a value of the ratio $d/b$ slightly different from that obtained from observations: a change in $\mu_{22}$ or $d/b$ alone would be inadequate. Further, the above considerations show that of the many combinations of values of the quantities $\mu_{22}$ and $d/b$ which might be taken in order to obtain curves passing through the observed points P and Q, the values given in the following table (involving the same value of the O-O force-constant $\mu_{22}$, which is common to both cases) seem best to give a good explanation of the observed facts for both crystals. (The force-constants are in such units as give the force in dynes when the unit of length is the Å.)

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* 'Roy. Soc. Proc.,' A, vol. 113, p. 696 (1927).

| | $\mu_{22}$. | $\mu_{12}$. | $d/b$. |
|---|---|---|---|
| $Al_2O_3$ .................... | 11·0 | 1·0 | $0{\cdot}51\ \pi/\sqrt{3}$ |
| $Fe_2O_3$ .................... | 11·0 | 2·0 | $0{\cdot}52\ \pi/\sqrt{3}$ |

8.4. The values of $d/b$ for $Al_2O_3$ and $Fe_2O_3$ derived from observations are approximately $0{\cdot}52\ \pi/\sqrt{3}$ and $0{\cdot}54\ \pi/\sqrt{3}$ respectively, so that the alteration in this quantity indicated in the above table is about 2 per cent. for $Al_2O_3$ and about 4 per cent. for $Fe_2O_3$. These alterations are within the limits of error of the observations (*cf.* table in § 2), as the following values indicate. For, the calculated value of $d$ for $Al_2O_3$, using $b = 1{\cdot}45$ Å and $d/b = 0{\cdot}51\ \pi/\sqrt{3}$, is 1·34 Å while the observed value is 1·37 Å ± 0·03; and similarly for $Fe_2O_3$ using $b = 1{\cdot}51$ Å and $d/b = 0{\cdot}52\ \pi/\sqrt{3}$, $d = 1{\cdot}42$ Å and the observed value is 1·44 Å ± 0·05. The agreement is very satisfactory.

However, an examination of fig. 4 indicates that it might be possible by decreasing $d/b$ to a larger extent, whilst leaving $\mu_{22}$ unchanged at its original value 17·6, to obtain curves which pass through the "observed" points P and Q respectively. (But it is to be noted that it cannot be stated without detailed examination that such a combination of values of $d/b$ and $\mu_{22}$ would result in a minimum value of the total energy $U_0 + U_m$ for values of $a_m$, $\alpha_m$ and $b$ close to the observed values, as has been observed above.) It seems clear, however, that the requisite decrease in $d/b$ would have to be about 10 per cent. This would mean, if we ascribe this decrease in $d/b$ to a decrease in $d$ alone whilst $b$ remains unchanged, that the Al (or Fe) ions would be practically equidistant from the six surrounding O ions. But Pauling and Hendricks,* as a result of accurate measurements, conclude that the Al (or Fe) ions are not equidistant from the six surrounding O ions, but are so arranged that three O ions are nearer than the other three. For instance, in $Al_2O_3$ the

* Pauling and Hendricks, *loc. cit.*

distances are $1 \cdot 990$ Å ± $0 \cdot 020$ and $1 \cdot 845$ Å ± $0 \cdot 015$. This experimental fact makes the assumption of such a large decrease in $d$ alone untenable. Further, if we consider this decrease in $d/b$ to be due to an increase in $b$ alone, the inequality in the distances of the O ions is very much increased; that is, taking $b = 1 \cdot 58$ Å in $Al_2O_3$ the distances of the O ions surrounding an Al ion are $2 \cdot 091$ Å and $1 \cdot 769$ Å. Such a large difference in the distances seems unlikely physically. Of course, we could avoid this large difference in the O-Al distances whilst retaining the value $b = 1 \cdot 58$ Å, by making $d$ smaller, but since this involves a further decrease in the ratio $d/b$, it cannot seriously be considered.

It is worthy of note also, that a value of $b = 1 \cdot 58$ Å corresponds to a value of $\lambda = 1 \cdot 58/4 \cdot 745$ or approximately $\frac{1}{3}$, which indicates that the O ions would be accurately in hexagonal close packing (*cf.* fig. 1). W. L. Bragg and G. B. Brown* in a paper on the structure of chrysoberyl have pointed out the similarity in the structures of the crystals BeO, $Al_2O_3$, $BeAl_2O_4$ and $MgAl_2O_4$, indicating that a common principle governs all four structures, namely, the hexagonal close-packing of the O ions at a distance of about $2 \cdot 7$ Å apart. Thus it would seem that in $Al_2O_3$ this arrangement of the O ions plays a predominant part in determining the structure of the crystal, but that there is a certain small distortion of the hexagonal close-packed arrangement, with the Al ions in some of the interstices of the structure. The considerations of this paper indicate that theoretically, in terms of the electrostatic and intrinsic repulsive ionic-forces which have been considered, an exact hexagonal close-packed arrangement of the O ions is not compatible with the observed size and shape of the crystal. Theoretically there must be some slight distortion from the close-packed arrangement (as indicated by the values of $d/b$ and $b$, *i.e.*, $d$ and $b$), and it has been shown that for the values of the force-constants $\mu_{22}$ and $\mu_{12}$ given earlier in this paragraph, a very good account can be given of the observed amount of the distortion and also of the other measurable quantities involved in the structures of the crystals, viz., $a_m$, $\alpha_m$ and $b$.

8.5. Finally the values of the force-constants $\mu_{12}$ and $\mu_{22}$ may be considered. The values $\mu_{12} = 1 \cdot 0$ for $Al^{+++}$ and $O^{--}$ ions, and $\mu_{12} = 2 \cdot 0$ for $Fe^{+++}$ and $O^{--}$ ions, might be taken as approximate values of these force-constants deduced by the methods of this paper. As has already been indicated the former value agrees with that obtained by using the relation (10) (*cf.* § 8.1), whilst the latter is somewhat larger than the value $1 \cdot 7$ found by J. E. Lennard-Jones and B. M. Dent for $Fe^{++}$ and $O^{--}$ ions. Further, the value $\mu_{22} = 11 \cdot 0$ for $O^{--}$

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* 'Roy. Soc. Proc.,' A, vol. 110, p. 34 (1926).

ions yielded by the considerations of this paper is much smaller than the value 17·6 obtained by the above authors. However, it appears that even such a big reduction in the value of this force-constant will not seriously affect the calculations on other crystals which they have previously made. For example, if we consider the crystal MgO and re-calculate the interatomic distance $a$ of the crystal, using the new value $\mu_{22} = 11 \cdot 0$ and taking the force-index to be 11, the value of $a$ so obtained is altered from 2·10 Å to 2·07 Å, while the observed value is 2·09 Å. And even this discrepancy can be nullified by a very slight increase in the value of $\mu_{12}$ for $Mg^{++}$ and $O^{--}$ ions; this is, in fact, the most important force-constant so far as concerns the statical equilibrium of the MgO crystal. Further, it is clear from the method of calculation† of the force-constants that they may in error to a large extent; for the force-constant for $O^{--}$ ions is calculated from the formula $\mu_{22} = (\rho^{--}/\rho)^{10} \cdot \mu_{00}$, where $\rho^{--}/\rho$ is the ratio of the diameter of the $O^{--}$ ion to that of the neon atom, and $\mu_{00}$ is the force-constant for neon ($n = 11$). But the value of $\rho^{--}/\rho$ given by Wasastjerna‡ is not very exact, and since this quantity has to be raised to the tenth power and multiplied by $\mu_{00}$, a small error in it may cause a large error in the resulting value of $\mu_{22}$.

It is therefore important that the accuracy of the values of the force-constants should be tested by considerations of the equilibrium of crystals, other than those used in the original determination of the force-constants, and particularly crystals such as those treated in this paper, for which the configuration of "absolute" minimum potential energy is fairly sensitive to changes in the values of the force-constants. It is therefore probable that a more accurate determination of the force-constants will be thus obtained, and as indicated above, such considerations for $Al_2O_3$ and $Fe_2O_3$ yield a value $\mu_{22} = 11 \cdot 0$ for the force-constant for $O^{--}$ ions.

With this additional information concerning $\mu_{22}$, it is of interest to re-consider the results obtained earlier for sodium nitrate, $NaNO_3$.§ It was found that by using the value $\mu_{22} = 17 \cdot 6$, a theoretical series of possible stable configurations of the crystal was obtained, which did not include the observed configuration. But it was shown that for various combinations of values of the force-constants $\mu_{12}$ for $Na^{+}$ and $O^{--}$ ions and $\mu_{22}$ for $O^{--}$ ions, a theoretical series of configurations could be found which did include the observed configuration. However, it was not possible, without additional evidence, to decide which of the many combinations of values was the correct one. Consequently the calculations have been repeated using the value $\mu_{22} = 11 \cdot 0$, and it has been found that the line of possible configurations on the $(a_m, \alpha_m)$ diagram almost exactly passes through the "observed" point for $NaNO_3$, if a value $\mu_{12} = 2 \cdot 9$ be used. The value of $\mu_{12}$ for $Na^+$ and $O^{--}$ ions given by J. E. Lennard-Jones and B. M. Dent is $2 \cdot 55$, so that the necessary alteration in this value is only about 14 per cent., which is reasonably satisfactory.

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† Lennard-Jones and Taylor, 'Roy. Soc. Proc.,' A, vol. 109, p. 485 (1925).

‡ 'Soc. Sci. Fenn. Comm. Phys. Math.,' vol. 1, p. 38.

§ Topping and Chapman, 'Roy. Soc. Proc.,' A, vol. 113, p. 658 (1927).

It is probable that similar calculations for the carbonate crystals $MgCO_3$ and $CaCO_3$ will also give fairly satisfactory results; that is, using the value $\mu_{22} = 11 \cdot 0$, a theoretical series of configurations can be found which includes the observed configuration, if for each crystal some reasonable change is made in the value of $\mu_{12}$ found by the above authors. But since these crystals do not provide a very good criterion for the determination of the force-constants, and particularly because of the complexity of the $CO_3$ (or $NO_3$) ionic group, and the uncertainty concerning the forces operative between the various ions of the group, it does not seem worth while to make the detailed calculations. However we may conclude that the results for $NaNO_3$ do not conflict with those for $Al_2O_3$ and $Fe_2O_3$, and the balance of evidence is in favour of some considerable reduction in the value of the force-constant $\mu_{22}$ for $O^{--}$ ions, as indicated above.

8.6. In conclusion the author wishes to express his best thanks to Prof. S. Chapman, F.R.S., for his advice and encouragement throughout the work, and to Prof. W. L. Bragg, F.R.S., for his help concerning some of the physical questions involved.

## LIST OF SYMBOLS USED IN THE PAPER.

$a$ = length of side of the equi-angular networks which lie in planes perpendicular to the trigonal axis of the crystal.

$c$ = distance between successive planes of O ions perpendicular to the trigonal axis.

$b\sqrt{3}$ = length of side of the triangle of O ions which surrounds each net-point.

$2d$ = distance between the two Al ions of the $Al_2O_3$ group around each net-point.

$\lambda = b/a$. $t = 2\pi a/3\sqrt{3}c$.

$\alpha$ = the characteristic rhombohedral angle of the crystal: it satisfies the relation $\operatorname{cosec}^2 \frac{1}{2}\alpha = 4\left(\frac{1}{3} + 4\pi^2/27t^2\right)$.

$\mu_{22}$ = force-constant involved in the assumed law of intrinsic repulsive force between $O^{--}$ ions, viz., $\mu_{22}r^{-11}$, where $r$ denotes distance.

$\mu_{12}$ = force-constant for $Al^{+++}$ and $O^{--}$ ions, corresponding to a law of force of the form $\mu_{12}r^{-11}$.

## *Summary.*

The considerations of this paper show that by postulating a form of the crystals in which the ions are regarded as point-charges between which electrostatic and certain intrinsic repulsive forces are assumed to be operative, a very good account can be given of all the observable quantities, that is, $a$, $\alpha$, $b$ and $d$, involved in the structures of the crystals $Al_2O_3$ and $Fe_2O_3$.

It is further indicated that theoretically an *exact* hexagonal close-packed arrangement of the O ions is incompatible with the observed values of the interatomic distance $a$ and the rhombohedral angle $\alpha$, and that there must be some small distortion from the exact arrangement. This distortion is indicated by the mutual distances of the ions of the $Al_2O_3$ groups which surround the lattice-points, that is, by the value of the distance $2d$ between the Al ions and the distance $b\sqrt{3}$ between the O ions of such an $Al_2O_3$ group. These results are in good agreement with experiment.

Also, estimates of the values of the force-constants for $Al^{+++}$ and $O^{--}$ ions, and for $Fe^{+++}$ and $O^{--}$ ions are found, and a value $\mu_{22} = 11$ for $O^{--}$ ions is obtained which is considerably less than that given by J. E. Lennard-Jones and B. M. Dent. Using this value of $\mu_{22}$, crystalline sodium nitrate has been reconsidered and reasonably satisfactory results have been obtained.

# *Elastic Constants of Fused Quartz. Change of Young's Modulus with Temperature.*

By H. D. H. Drane, M.Sc., Ph.D.

(Communicated by Lord Rayleigh, F.R.S.—Received August 11, 1928.)

When fused quartz is heated, its elastic constants for stretch shear and bulk change all increase, a sharp distinction in behaviour from that of most other elastic solids.

An elastically-stretched fibre becomes shorter upon heating, and a strained torsion member reduces its twist for a given twisting effort; and so forth. The changes of shear modulus with temperature have been studied in detail (22 to 98° C.) by Threlfall* and later by Horton† to about 1000° C., who used methods of experiment based upon the changes in period upon heating, of a torsional pendulum having fused quartz as the elastic member. The results of Horton's experiments showed a continuous increase in modulus up to about 880° C. beyond which temperature the modulus rapidly diminished. At 880° C. the modulus was 5·9 per cent. greater than at 15° C. and the mean rate of increase up to 500° C. was $0 \cdot 85 \times 10^{-4}$ per degree Centigrade. The increase is more rapid at lower temperatures, thus, in the interval 20 to 100° C. mean rate of increase per degree Centigrade was found by Horton to be $1 \cdot 25 \times 10^{-4}$, which is in good agreement with the earlier determinations made by Threlfall. At still lower temperatures, and using the same method of torsional oscillation, Guye and Einhorn-Bodzechowski‡ showed that the mean temperature coefficient in the interval −194° C. to 0° C. is $1 \cdot 46 \times 10^{-4}$ per degree Centigrade, and that there is no major discontinuity in behaviour in this range.

The information concerning the changes in Young's modulus of fused quartz is not so complete or exact. Only a cursory investigation upon the subject has been made by Lees and his co-workers§ while studying the effect of temperature upon the Young's modulus of various metals. In this work, large (more than 100 per cent.) changes were reported on the modulus in the interval 20 to 600° C., together with the display of maximum and minimum points, but such large changes and irregularities have not at all been confirmed by my present investigations. The method used by Lees was based upon the changes in elastic deflection suffered by a small (5 cm. length) cantilever of silica end loaded, or by a specimen of silica fibre deflected under its own weight. Observations were made directly of the movement of the end of the specimen, which was arranged within a small tube furnace, about 7 cm. long by 3 cm. diameter. While correctly allowing the change of modulus to be stated as an increase with rise in temperature, the experimental details did not permit a high accuracy to be realised. It would appear probable that some of the irregular effects observed by Lees in the experiments with silica must be attributed to the method adopted for support of the test specimens.

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* 'Phil. Mag.,' vol. 30, p. 99 (1890).

† 'Roy. Soc. Proc.,' A, vol. 74, p. 401 (1905).

‡ 'Arch. Sci. Phys. Nat.,' vol. 4, p. 41 (1916).

§ 'Proc. Phys. Soc. Lond.' vol. 36, p. 405 (1923).

The changes in Young's modulus over any range of temperature are most conveniently studied with a specimen in the form of a cantilever beam. A simple extension member demands a long uniformly-heated furnace with all its attendant difficulties—as Threlfall (*loc. cit.*, p. 115) has already pointed out—whereas the cantilever specimen can be small and kept at a uniform temperature without using a furnace of unusual size or complexity. The experimental arrangements used in the present investigations are shown in fig. 1 (*a*) and 1 (*b*) below.

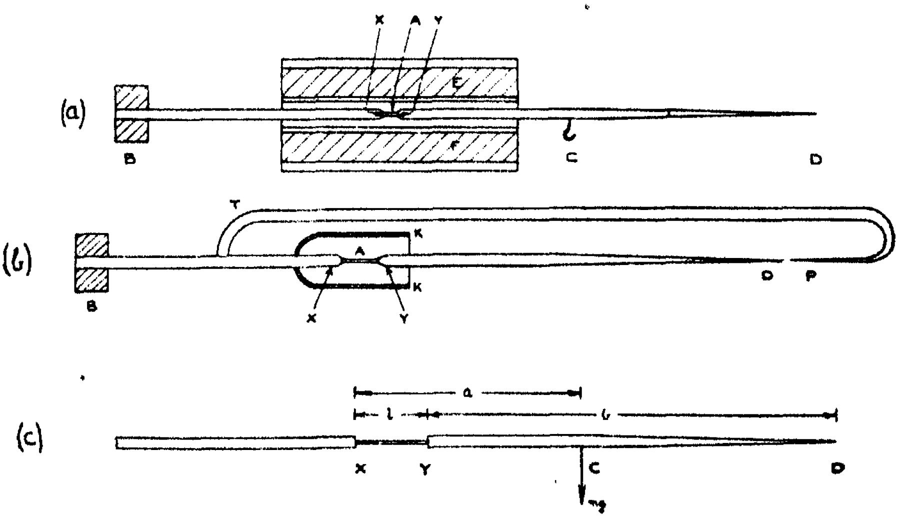

FIG. 1.

The essential observations were of the deflection at a fixed temperature (15° C.) and the changes in deflection of the small loaded cantilever A of fused quartz as the temperature of the specimen was varied. The method being static is suited to use only within a temperature range where viscous motion in the specimen is not apparent. With the dimensions of the specimens and the loadings used the maximum temperature up to which measurements could be made accurately was about 700° C. For measurements above room temperature the arrangement shown in fig. 1 (*a*) was used. The specimen A was in the form of rod approximately 1·5 mm. diameter by 2 to 3 cm. in length and was attached by fusion at its ends to the tubes BX and YD. These were also of fused quartz and neither was measurably deformed with the loadings used. At B the left-hand supporting tube was clamped as rigidly as permissible. No vertical displacement was possible, but slight pivoting occurred in the plane of the diagram about a point within B. This was measured at X and applied in the calculation of the total elastic deflection—measured at D—suffered by the specimen. YD served as a pointer to magnify the motion of the end of the test specimen, and at D, and carried a fine sighting fibre arranged vertically which moved in the field of view of a reading microscope. Before assembly the hook C was attached by fusion immediately below the centroid of YD, and YD together with C was weighed before fusion to the specimen. The attachment of this hook was thin and flexible, so that weights hung from it were applied truly at the centroid of YD. With this arrangement the latent initial deflection at D, due to the weight of the pointer rod YD, was easily determined by adding additional weight at D. The usual total loadings arranged at C were between 10 and 20 grs. EF represents a small wire-wound silica tube furnace 2·5 cm. internal diameter by 30 cm. long. During an experiment the ends of this furnace were closed with asbestos shields carrying short (2 to 3 cm.) lengths of silica tube, which allowed free movement of the support and pointer rods but largely prevented air circulation. The overall dimensions BD was about 60 cm.; YD, 40 cm. The temperature of the specimen was measured within 1° C. by a rare metal thermocouple and millivoltmeter combination which was specially calibrated for this work at 100° C. (steam point), 327° C. (lead melting point), and 575° C. ($\alpha - \beta$ quartz transformation point). The hot junction of the thermocouple was placed within 1 mm. of the specimen and good temperature equilibrium was obtained with heating rates less than 3° C. per minute.

To perform an experiment C was loaded by brass weights, suspended in water to damp oscillations, so that the total elastic deflection measured at D was about 3 cm., the apparatus being arranged so that the rod YD was horizontal when fully deflected ready for measurement. Movement of D upon heating was observed in the eyepiece of a reading microscope, which measured units of $3 \cdot 06 \times 10^{-3}$ cm., and with which estimates to $3 \times 10^{-4}$ cm. could be made. In all experiments the initial observation of the induced elastic deflection due to the loading was made at room temperature and corrected for any material deviation from 15° C.; thereafter upon heating only the changes in deflection were observed.

For the experiments at low temperatures the apparatus was modified as shown in fig. 1(*b*) by fitting a cup KK of fused quartz around the specimen A and fusing this to the rod BX. A rigid tube T was fused on to BX below its junction with the cup mentioned above and drawn out to a point P. This point was arranged to be in coincidence with D when YD hung vertically below A. The apparatus was then reversed so that P was uppermost, and deflected from the vertical so that D moved away from P. The distance PD was measured and the movement of D observed as previously, when K was filled with liquid oxygen. The angular deviation of the pointer rod YD from the vertical was also measured and the experiment repeated for several different angular positions of the apparatus. YD in this assembly was about 55 cm. long, and the angular displacements used in the experiments were between 15° and 45° from the vertical. Referring to the diagram shown in fig. 1*c* the deflection observed at D for a loading of mg. at C may be written

$$\Delta = \frac{mg}{2\mathrm{EI}}\left[al^2 - \frac{c^3}{3}\right] + \frac{mg}{\mathrm{EI}}\left[abl - \frac{bl^2}{2}\right],$$

the two terms representing the deflection of the specimen at Y and the magnified sweep of D about Y due to the inclination of the end of the specimen respectively. I is the moment of inertia of the specimen regarded as uniform throughout its length and E is the Young's modulus. The dimensions *a*, *b* and *l* are shown in the diagram fig. 1 (*c*). With the dimensions of the apparatus used, the first of these two terms accounted for from 2½ to 4 per cent. of the observed motion at D, and the main effects of the dimensional alterations in the specimen and the pointer rod may be accounted for as below

$$\mathrm{E}_{t_2}/\mathrm{E}_{t_1} = (1 + \delta/\Delta_{t_1})^{-1}\left\{1 - \tfrac{3}{2}\alpha\,(t_2 - t_1)\right\},$$

where $\delta$ is the increase in deflection observed in the temperature interval denoted by the subscripts $t_1$ and $t_2$. For a positive temperature increment, $\delta$ is negative. YD is regarded as heated for half its length—a close approximation, $\alpha$ is the mean coefficient of linear expansion of fused quartz in the range considered. The correction implied by the second bracket, and which accounts for the dimensional changes occurring, is small. For the interval 15 to 700° C. it requires a correction of $-0 \cdot 05$ per cent. to be applied to the values of the modular ratio determined by the approximate relationship $E_{t_2}/E_{t_1} = (1 + \delta/\Delta_{t_1})^{-1}$. The requisite correction has been applied to the values shown in Table I. With the inclined arrangement of the apparatus for measurements at low temperatures the following relationship may be shown to apply

$$E_{t_2}/E_{t_1} = (1 + \delta/\Delta_{t_1})^{-1} (1 + \delta \cot \theta/b)\{1 - 4\alpha(t_2 - t_1)\},$$

where $\theta$ is the angle of deviation of the pointer rod from the vertical and $b$ its length. The correcting factor for dimensional changes appears here as $1 - 4\alpha(t_2 - t_1)$ since only the specimen undergoes dimensional alteration, but the correction implied is particularly small—in the interval concerned, 15° C. to −183° C., fused quartz exhibits a minimum length—and amounts only to 0·002 per cent. in this interval.

Table I.

| Temperature, $\theta$° C. | Ratio $E_\theta/E_{15}$. | Mean temperature coefficient from 15° C. | Mean temperature coefficient between successive temperatures. |
|---|---|---|---|
| −183 | 0·9695 | $1·53 \times 10^{-4}$ | $1·60 \times 10^{-4}$ |
| 15 | 1·000 | — | 1·65 |
| 100 | 1·0140 | $1·65 \times 10^{-4}$ | 1·38 |
| 200 | 1·0280 | 1·51 | 1·26 |
| 300 | 1·0410 | 1·44 | 1·10 |
| 400 | 1·0525 | 1·36 | 0·95 |
| 500 | 1·0625 | 1·29 | 0·84 |
| 600 | 1·0715 | 1·22 | 0·70 |
| 700 | 1·0790 | 1·16 | |

Five test specimens were used in the various experiments performed, made up from three specimens of quartz of differing geological origin but no systematic differences in behaviour were observed. The irregularities which were observed lay within the limits got in making re-tests upon an individual specimen. The general behaviour was a continuous increase in modulus from —183° C. to beyond 700° C. and the averaged performance is shown quantitatively in the table below and by the continuous curve in fig. 2.

In view of the known expansion behaviour of silica at low temperatures, the continuity of the change in modulus between —183° C. and room temperature was examined particularly so far as the experimental arrangements permitted. Upon each cooling to —183° C. and subsequent heating of the specimen, the drift of the pointer was observed closely but no stationary point was shown which a minimum value of the modulus would require. The value observed at —183° C. is in fair agreement with the rate of change observed above 15° C., but closer inspection of the values shown in Table I suggests some irregularity of behaviour between room temperature and —183° C. The minor and unsystematic differences in behaviour at higher temperatures observed in passing from specimen to specimen were apparent in re-tests upon any one specimen, but sufficient experimental evidence is not yet available to give a clear exposition of the mechanism of theseir regularities. They are certainly not due to any visible phase change in the specimen. The most noteworthy effect was observed in re-tests of the various specimens, and was an apparent increase in viscosity after heating. This is exemplified by the recorded points of turnover in the experiments below. In the successive experiments shown in Table II and except for heats 2 and 7, heating was continued until the deflection of the specimen became stationary and thereafter increased continuously due to viscous flow. The rate of distortion at 750° C. after heat No. 10 was per minute 0·027 per cent. of the total elastic deflection,

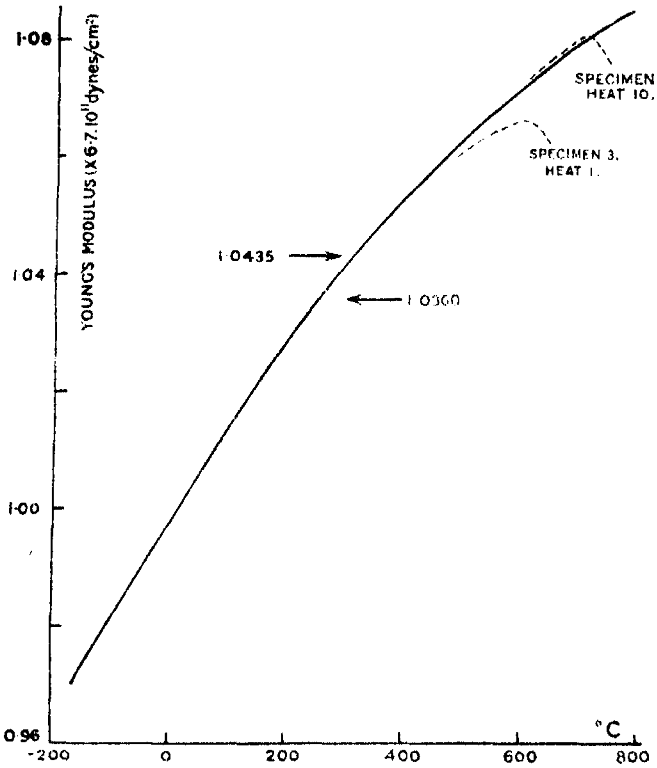

Fig. 2.

and in the earlier heats this rate was approximately realised at correspondingly lower temperatures roughly in each case 30° C. above the temperature given as point of turnover. At 600° C. after heat No. 10 the viscous displacement did not amount to 0·01 per cent. of the total elastic deflection for a period of 2 hours.

Table II.

| Sequence of heating. | Point of turnover °C. | Maximum temperature °C. | Ratio $E_{300}/E_{15}$. | Induced elastic deflection at 15° C. (fixed load). |
|---|---|---|---|---|
| | | | | cm. |
| 1 | 605 | 650 | 1·040 | 1·980 |
| 2 | – | 420 | 1·0402 | 1·970 |
| 3 | 650 | 676 | 1·0365 | 1·985 |
| 4 | 690 | 740 | 1·0410 | 1·990 |
| 5 | 705 | 762 | 1·0390 | 1·995 |
| 6 | 735 | 770 | 1·0435 | 1·960 |
| 7 | — | 332 | 1·0415 | 1·955 |
| 8 | 725 | 760 | 1·0387 | 1·960 |
| 9 | 715 | 756 | 1·0415 | 1·970 |
| 10 | 720 | 765 | 1·0415 | 1·967 |

As shown in Table II above, semi-permanent changes were also observed in the value of the modulus after cooling to room temperature and these are illustrated by the successive values of the induced elastic deflection at 15° C. with a fixed load. A part of these changes is to be attributed to dimensional alteration of the specimen during viscous displacement under load, but this agency was secondary to the thermal treatment of the specimen. Slight but measurable changes in the modulus were observed after heating only to 420° C., see column 5, Table II.

There appears to be some close relationship between the optical anomalies found by Rayleigh* in examining specimens of vitreous silica, and the irregularities in mechanical behaviour found in the present investigation. These optical anomalies displayed many of the characters observed by Lehmann in studying "liquid crystals," and the present behaviour is in agreement with the occurrence of such changes. It is not suggested that fused quartz exists in different allotropic forms which change over with the display of marked discontinuity in ordinary physical properties—this in fact is contrary to experience. The differences, however, between any co-existing phases appear to be shown up best by optical and particularly by mechanical methods of test; and a co-related optical and mechanical investigation offers itself as a useful method

* 'Roy. Soc. Proc.,' A, vol. 98, p. 284 (1921).

of enquiring into the mechanism of these changes. This general aspect of the behaviour of fused quartz appears not to have received the attention in the literature which it deserves. Apparently the semi-permanent changes in modulus which were induced by the thermal treatments used in the present investigations are much less than can be realised. Various authors have made determinations of Young's modulus for fused quartz at room temperature upon isolated groups of specimens, obtaining average values which range from a minimum of $5 \cdot 2 \times 10^{11}$ dynes/cm.$^2$, up to $7 \cdot 15 \times 10^{11}$ dynes/cm.$^2$.

The values which are given are summarised below:

Table III.

| | | |
|---|---|---|
| Threlfall | $5 \cdot 2 \times 10^{11}$ dynes/cm.$^2$ | 'Phil. Mag.,' vol. 30, p. 99 (1890). |
| Boys | $6 \cdot 0 \times 10^{11}$ dynes/cm.$^2$ | 'Phil. Mag.,' vol. 30, p. 118 (1890). |
| Auerbach | $7 \cdot 15 \times 10^{11}$ dynes/cm.$^2$ | 'Ann. Physik,' vol. 39, p. 116 (1900). |
| Schulze | $6 \cdot 2 \times 10^{11}$ dynes/cm.$^2$ | 'Ann. Physik,' vol. 4, p. 384 (1904). |
| Heymans and Allis | $6 \cdot 9 \times 10^{11}$ dynes/cm.$^2$ | 'J. Math. Phys.,' vol. 2, p. 216 (1923). |
| Drane | $6 \cdot 7 \times 10^{11}$ dynes/cm.$^2$ | Not published. |

The temperatures at which these measurements were made are not generally specified more closely than "room temperature," and have been presumed to lie in the range 15 ± 3° C. Possible temperature variations, however, offers no explanation of the real differences which exist.

The English experiments, upon which the results quoted above are based, were made upon fibres of fused quartz. Thus Threlfall (*loc. cit.*, p. 116) deduced values for E from the deflection of fibres loaded centrally as simple beams between supports 4 cm. apart. His final result for E was $5 \cdot 1785 \times 10^{11}$ dynes/cm.$^2$ but in view of later work this close specification of the value of the modulus appears untenable. In a footnote to the paper by Threlfall, Boys put forward the averaged value of $6 \cdot 0 \times 10^{11}$ dynes/cm.$^2$ which he had obtained from many experiments upon quartz fibres in a small extensometer. In this the fibre under test was held vertically and the load applied to the upper end of the fibre. The load was measured by the deflections of a right-angled metal member carrying a gravity bob, working on knife edges and suitably attached to the upper end of the fibre. The load was varied by retracting the lower end of the fibre by a micrometer screw, with which a microscope, reading on the upper end of the fibre, travelled.

The German investigators used more massive specimens. Auerbach experimented upon flat plates and lenses, and determined E indirectly from the elastic indentation produced in his specimens under stated loadings. His method of reduction of results presumed a value of 0·20 for Poisson's ratio (it should be 0·12 to 0·14) and is in error to some extent on this account. The error is not great since Poisson's ratio $\sigma$ is involved as a factor of the form $(1 - \sigma^2)$, and the value shown in Table III above has been corrected using $\sigma = 0 \cdot 13$. Schulze criticised Auerbach's assumption of the value 0·20 for Poisson's ratio and redetermined $E$ and the torsion modulus, by experiments upon the mechanical oscillations induced in a flat polished bar of fused quartz, the frequency of vibration being determined by reference to calibrated tuning forks. A more direct and exact method was used by Heymans and Allis, who studied the transverse and longitudinal curvature of a bent polished beam of fused quartz by an interferometric method. The results in Table III by Drane were obtained by dead loading long (up to 2M) fibres of fused quartz, which were later cut and measured accurately throughout their length, and also upon flat strips and rods of silica arranged as beams; none of these specimens was polished and all the beam experiments were reduced by graphical methods, which accounted properly for the slight variations in dimensions of the specimens. Although the experimental methods used in some of the examinations above have been indirect, their principle is sound, and, in reviewing the results, one is forced to the conclusion of actual variability in the modulus. There remains as a problem the specification of the precise thermal and mechanical treatment necessary to yield a specimen of fused quartz with fixed mechanical and optical characteristics.

In conclusion the author would like to express indebtedness to Mr. G. N. Peel, B.Sc., and Mr. R. Brown of this laboratory for recording many of the observations entailed in these investigations, also to the Directors of The Thermal Syndicate, Ltd., for sustained interest and the permission of publication.

# *The Pressures of Gaseous Mixtures. II—Helium and Hydrogen, and their Intermolecular Forces.*

By C. W. Gibby, Ph.D., C. C. Tanner, Ph.D., and Irvine Masson, D.Sc.,
Chemistry Laboratories, University of Durham (Durham Division).

(Communicated by F. G. Donnan, F.R.S.—Received October 17, 1928.)

## *Statement of the problem.*

## § 1.

The work discussed in this paper was begun in 1924 in London, and was later on resumed in Durham. It forms part of an investigation which began eight years ago, of which the purpose was to gain information from a new quarter about intermolecular action; and the first part was published in 1923 by Masson and Dolley.* In that part of the work, which dealt with the compressibilities of argon, of oxygen, of ethylene, and of a number of mixtures of each pair of these gases, a systematic study was made of deviations from Dalton's law of partial pressures. It was possible to exhibit the cohesion of the molecules of one gas with those of another gas; and to prove, without using any special theory, that this type of cohesion is neither caused nor influenced by the possibility of chemical action between the atoms composing two colliding molecules. Thus this kind of cohesion differs from that which gives rise to unimolecular films, where the cohesion is chiefly traceable to the specific action of some particular atom within one molecule upon a particular atom in another, or in a surface. The bearing of this distinction has been discussed elsewhere,† and thermodynamic aspects of the first paper have been recently dealt with by other authors.‡ Meanwhile, it becomes clear from the results of that paper that any theory, proposed to explain the van der Waal's cohesion between molecules of two different chemical kinds, need not invoke any types of force beyond those that could explain cohesion in a single pure gas. The present paper deals experimentally and theoretically with such forces.

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* 'Roy. Soc. Proc.,' A, vol. 106, p. 524 (1923).

† Masson, 'Trans. Faraday Soc.,' vol. 24, p. 168 (1928).

‡ Gibson and Sosnick, 'J. Amer. Chem. Soc.,' vol. 49, p. 2172 (1927); Randall and Sosnick, *ibid.*, vol. 50, p. 967 (1928).

## § 2.

The first stage of the present experiments (1924) with helium and hydrogen indicated a new property in gases; for the data showed a certain range of mixtures of these two as being more incompressible than either constituent; a maximum being suggested at about 30 per cent. of helium in the mixture. Incidentally, this displaced hydrogen from its position as the least compressible gas. The effects were, however, slight; and, chiefly in order to test their genuineness, we resumed the work in 1926, and improved the methods in various ways. One result has been to confirm the new property, though the effect is very small; and meanwhile, Lennard-Jones* has independently noticed a similar effect in the experimental data of Holborn for a mixture of neon and helium; and in his recent theoretical work on gaseous mixtures he has been able to show it as a special case of the general properties of gases. The same general treatment proves to be applicable to the work we have done, as will be shown.

The experiments now described were on the compressibilities, up to 125 atmospheres, of helium, hydrogen, and 10 mixtures of the two at 25° C.; and of both pure gases and one mixture at seven temperatures from 25° to 175°. The data afforded by these gases are simpler to examine quantitatively than were those of the former paper; for all the compressibility isotherms ($pv$ plotted against $p$) prove to be straight lines, $pv$ increasing with pressure according to the simple equation

$$pv = a + bp. \tag{1}$$

In this, $v$ is the volume of the gas-sample in terms of its volume at S.T.P., and $a$ and $b$ are constants for the particular gas at the given temperature. Thus the coefficient $b$ gives the deviation from Boyle's law. Only with pure hydrogen at the lowest temperature (25°) is there a very slight flexure, requiring a third term $cp^2$.

Our chief concern in this paper is to interpret our coefficients $b$, the slopes of the isotherms, in terms of intermolecular forces.

## § 3.

Before the results are discussed, it should be recalled that the deviations of pure hydrogen and of pure helium from Boyle's law are not only both in the same direction, but are nearly the same in amount; for instance, the values of $pv$ at 100 atmospheres and 25° are, for hydrogen, 1·157, and for helium

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* 'Nature,' vol. 119, p. 459 (1927).

1·142; corresponding with $b \times 10^4 = 6 \cdot 56$ and $5 \cdot 10$ respectively. Thus, in mixtures ranging from pure hydrogen to pure helium, there is only a small change of experimental properties—about 1 per cent.—to explore; and in order to get useful figures, experimental accuracy is important. In our work, we have had to restrict ourselves to quite small quantities of gas for each series of measurements, usually about 7 c.c. at 1 atmosphere, either pure or made up by mixing two smaller measured quantities. Nevertheless, we have satisfied ourselves that adequate accuracy has been secured to limit the uncertainty in the resulting figures for $b$ to about 1 per cent. At our higher temperatures there is an occasional aberration, to be duly noted in its place.

### *Discussion of results.*

### § 4.

For a *pure* gas in which $pv = a + bp$, the coefficient $b$ measures the deviation of the gas from the ideal state; and the meaning of $b$ thus embodies the results of forces that act between molecules all of which, in a pure gas, are of one kind only, like acting upon like. The coefficient for one pure gas will therefore be particularised as $b_{11}$; that for some other pure gas as $b_{22}$; and these are directly measurable. For a gaseous *mixture* whose compressibility is given by a similar equation

$$pv = a_m + b_m p, \tag{2}$$

the experimental coefficient $b_m$ clearly represents a more complex set of happenings than does $b$ for a pure gas. For, in the mixture, the two types of molecular encounter that occur in each pure gas, like with like, still go on; and so $b_{11}$ and $b_{22}$ remain to contribute towards making up $b_m$; but there is now an additional type of encounter, namely that between unlike molecules, which also contributes. The specific effect, not directly measurable, of encounters of this type will be denoted $b_{12}$. The actually measured $b_m$ of equation (2) is then regarded as composite, made up of three constants $b_{11}$, $b_{22}$ and $b_{12}$. Naturally, the proportion in which these three specific agencies contribute in constituting $b_m$ will be decided by the numerical proportions in which the two kinds of molecule are present in the mixture. Different mixtures of a given pair of gases will have differing $b_m$'s, determinable by direct experiment; but all of the mixtures of this pair, at a given temperature, whatever their compositions, should have one and the same characteristic $b_{12}$, if $b_{12}$ could be disentangled and evaluated.

Now, opportunely for this work, Lennard-Jones* has shown quite recently, and for the first time, how $b_{12}$ should be derivable from $b_m$, $b_{11}$ and $b_{22}$; the sole assumption being that around each molecule the field of force, whatever its nature, is spherically symmetrical. On this supposition, it is shown that

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* 'Roy. Soc. Proc.,' A, vol. 115, p. 334 (1927).

$$b_m = b_{11}x_1^2 + 2x_1x_2b_{12} + b_{22}x_2^2, \tag{3}$$

where $x_1$ and $x_2$ denote the molecular proportions of the two gases in the mixture; that is, $x_1 + x_2 = 1$. Hence

$$b_{12} = \{b_m - (b_{11}x_1^2 + b_{22}x_2^2)\}/2x_1x_2, \tag{4}$$

in which all the terms on the right-hand side are measurable by experiment. Lennard-Jones was able to quote Verschoyle's data* for three mixtures of nitrogen with hydrogen, at 0° and at 20°, as supporting equation (3); suitable values for $b_{12}$ being chosen, Verschoyle's figures for $b_m$ were reproduced with very fair success. The form of (3) also showed that a pair of gases which have suitable $b_{11}$ and $b_{22}$ might yield, when mixed, a value of $b_m$ greater than either —the effect referred to in § 2—and confirmation of this was found in Holborn and Otto's measurements upon a mixture of neon with helium.

Our own results afford more extended material for a test, and the facts may first be summarised.

## § 5.

In fig. 1 are shown, plotted in a very open scale, the observed values of $b$ for 12 compositions from 0 to 100 per cent. helium, all at 25° C. The height of the circle around each point is a guide to the probable error in $b$, arising from the several hundred observations that go to form a single point. One or two points possibly display a slight systematic error in the series which each embodies; but even with these, the curve shown expresses the data satisfactorily. Near 20 per cent. helium is drawn the very slight increase in $b$, compared with that of pure hydrogen, to which reference has already been made. The constants $a$ are recorded in a later table.

For connecting the results with the form of presentation adopted in the earlier paper, it may be remarked that all of these mixtures can be shown to deviate from Dalton's law of partial pressures; here, in the sense of yielding actual pressures higher than the additive figures. The deviation can be shown to be at its maximum in mixtures containing 50 per cent. of each constituent, where it reaches, at 25°, about 4 per cent. of the ideally additive pressure.

Comparing now the data of fig. 1 with theory, we may assign some fixed value to $b_{12}$ in equation (3) and deduce, from the observed values of $b$ for the

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* 'Roy. Soc. Proc.,' A, vol. 111, p. 552 (1926).

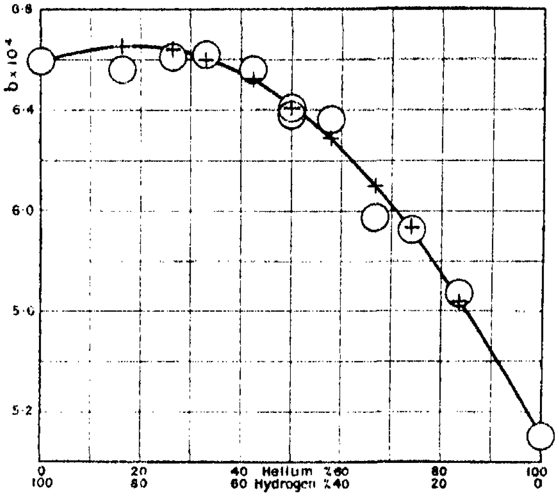

FIG. 1.—Helium-Hydrogen Mixtures: Variation of $b$ at 25° with Composition.

pure gases, what the variable $b_m$ should be for each experimental mixture. The calculated figures corresponding with a selected value

$$b_{12} = 6 \cdot 98 \times 10^{-4} \text{ for He} - \text{H}_2 \text{ at } 25^\circ$$

are marked as crosses in fig. 1, and the curve, already noted as satisfying the experimental points, was drawn through the calculated ones. The latter are also given in row iii of Table I, underneath the observed values in row ii: and it will be seen that the divergences only once reach 2 per cent., and the rest are well within the experimental error. A second test, the converse of the other, is to calculate $b_{12}$ for each experimental point, using equation (4), when a constant should be obtained. This puts a severe strain on the experiments, as it accumulates in $b_{12}$ any experimental errors present in $b_{11}$, in $b_{22}$, in $x_1$ and in $x_2$. In view of this, the results, forming row iv of Table I, are by

Table I.—Helium — Hydrogen at 25·0°.

$$pv = a + bp.$$

| i. Per cent. He | 0 | 16·26 | 26·40 | 33·00 | 42·42 | 50·06 | 50·11 | 57·54 | 66·64 | 73·99 | 83·49 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ii. $10^4 b$ obs. | (6·59) | 6·56 | 6·61 | 6·62 | 6·56 | 6·41 | 6·38 | 6·36 | 5·97 | 5·92 | 5·67 | 5·10 |
| iii. calc. | — | 6·66 | 6·64 | 6·60 | 6·51 | 6·41 | 6·41 | 6·29 | 6·10 | 5·92 | 5·66 | — |
| | | | | | | | | | | | | |
| iv. $10^4 b_{12}$ calc. | — | 6·62 | 6·91 | 7·02 | 7·07 | 6·98 | 6·92 | 7·13 | 6·68 | 6·97 | 7·02 | — |

no means unsatisfactory; they range about an arithmetic mean of $6 \cdot 93 \times 10^{-4}$, the greatest divergencies from this being less than + 3 per cent. and − 4 per cent. (Note that row iv is not to be compared with rows ii and iii.)

We conclude from this that our measurements bear out very well the assumption that the intermolecular forces in helium and hydrogen are spherically symmetrical about each molecule. Further knowledge of these forces is afforded by the next set of results.

## § 6.

The influence of temperature upon the constants of the isotherms was now studied, by measuring the compressibilities of the two pure gases, and of an equimolecular mixture, at or near 25°, 50°, 75°, 100°, 125°, 150°, 175°; the observations at each temperature being eventually expressed in the same form as those already reviewed (equations (1), (2)).

Within this temperature-range, the coefficient $b$ for helium was found to fall with rising temperature; for hydrogen, on the other hand, it rises, apparently to a maximum not far from 130°. With the 50 : 50 mixture, the values lie between those of the two gases, and they tend on the whole to fall slightly with rising temperature. When a solid diagram is constructed so as to show $b$, temperature, and composition, it appears that the maximum property of $b$, shown by mixtures near 20 per cent. helium at 25°, would vanish at temperatures above this, and would become more plainly manifest at temperatures rather lower than those which we have used. In some of the series at higher temperatures the accuracy was less than usual (see Table V at end), apparently owing to temperature-gradients in the compressor; and in Table II are therefore given the values of $b$ observed at the different temperatures, and in addition, for each gas, those read on the simplest smooth curve drawn through them.

Our results for the two pure gases have been carefully collated with those of other workers upon helium or upon hydrogen, chief of whom are Onnes and his collaborators at Leiden and Holborn and Otto at Charlottenburg. As to hydrogen, at 25° our values would necessarily agree with Holborn and Otto's, for we adopt these as our standard of reference. At higher temperatures, we obtain results which practically lie on the curve joining their data for 0°, 50°, 100°, and 200°. Our figures indicate that $b$ for hydrogen reaches its maximum probably within 10° of 130°.

As to helium, our values for $b$, excepting an erratic point at 150°, run closely below Holborn and Otto's curve, and parallel with it. We have not been

Table II.—Helium, Hydrogen, and 1 : 1 Mixture.

Values of $10^4 b$ in $pv = a + bp$. ($v = 1$ at S.T.P.)

| i. Temperature, °C. | 25·0° | 50·0° | 75·0° | 100·4° | 125·4° | 150·3° | 175·0° |
|---|---|---|---|---|---|---|---|
| i. Helium : observed | 5·10 | 5·07 | 5·02 | 4·86 | 4·94 | 4·62 | 4·87 |
| smoothed | 5·10 | 5·07 | 5·02 | 4·97 | 4·90 | 4·83 | 4·77 |
| ii. Hydrogen : observed | (6·59) | 6·71 | 6·86 | 6·93 | 7·02 | 6·93 | 6·87 |
| smoothed | 6·59 | 6·73 | 6·85 | 6·93 | 6·97 | 6·96 | 6·92 |
| iii. Mixture : observed | 6·41 | 6·44 | 6·37 | 6·43 | 6·20 | 6·41 | 6·20 |
| smoothed | 6·42 | 6·42 | 6·41 | 6·38 | 6·34 | 6·29 | 6·23 |
| iv. $b_{12}$ calc. from observed points | 6·98 | 6·99 | 6·80 | 6·97 | 6·42 | 7·04 | 6·53 |
| $b_{12}$ calc. from smoothed points | 7·00 | 6·94 | 6·88 | 6·81 | 6·75 | 6·69 | 6·63 |

able to trace a cause for the slight difference (*e.g.*, $b = 5{\cdot}07 \times 10^{-4}$ at 50°, where Holborn and Otto find 5·236), which ought to be outside our experimental error. Nevertheless, the fact that our curve is intermediate between those of Leiden and Charlottenburg in our range of temperature shows that our results have not been affected by any serious error. It should, at the same time, be noted that in another range, at temperatures below —100°, Onnes's values for the $b$ of helium differ very markedly and systematically from those of Holborn and Otto.*

## § 7.

It has already been shown that the field of force around each molecule of these gases is spherically symmetrical; and we may now go further, to specify the nature of these fields. There are three fields, namely, that involved in an encounter between 2He, that between $2H_2$, and that between He and $H_2$. The relation of the last-named to the other two will also be considered.

We make use of the valuable contributions to the kinetic theory which Prof. Lennard-Jones† has made during the last four years, including its recent extension to gaseous mixtures. Only such parts of his theory will here be mentioned as are needed for following its application to our results.

Dealing with a pure gas, Lennard-Jones treats an encounter between a pair of molecules as if it were governed by two superposed forces, the one of attraction and the other of repulsion. The fields are presumed to be spherically symmetrical around the centre of each molecule. The two forces are treated in the analysis as if each had its own distance-law and force-constant. Thus the *nett* force of cohesion between two similar molecules is given by

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* *Cf.* Holborn and Otto, 'Z. Physik,' vol. 30, p. 320 (1924), where a comparison is made and references are given.

† 'Roy. Soc. Proc.,' A, vol. 106, pp. 441, 463 (1924); vol. 107, p. 157 (1925); vol. 112, p. 214 (1926); and vol. 115, p. 334 (1927).

$$\text{Nett force} = \lambda_m . r^{-m} - \lambda_n . r^{-n}, \qquad (5)$$

where $r$ is the distance between the molecular centres, $\lambda_m$ and $\lambda_n$ are the constants respectively of the attractive component and of the repulsive, and $m$ and $n$ are the corresponding distance-law indices. Each pure gas is allowed its own characteristic values of $m$ and of $n$ (which cannot be less than 4) and of the force-constants.

Clearly these forces ought to represent, *inter alia*, the deviations of a gas from the ideal state; and they should therefore be connected with the coefficient $b$ of a pure gas to which $pv = a + bp$ is applicable. This correlation has been accomplished by Lennard-Jones. He was able to represent $b$ theoretically as a complex function of a function of temperature, such that the way in which $b$ depends upon T should be determined by the values of the distance-law indices, $m$ and $n$, in equation (5). Accordingly, for a given molecular model (defined by the values of $m$ and $n$), two functions can be numerically computed, without reference to experiments, and plotted against each other; the same can be done for each of a variety of models; and the resulting curves can then each be compared with the actual curve which shows the experimental change of $b$ with temperature. The theoretical curve whose shape is found to match the shape of the experimental curve thus decides which model is best appropriate to the particular gas. Finally, by making the curve-comparison a quantitative one, the force-constants, $\lambda$, for that model and that gas can also be evaluated. In this way the theory, embodying (5), has been shown by its author to be remarkably adequate, for a number of gases; and his extension of it to crystals has been no less successful.

For a gaseous mixture, precisely the same theory applies, except that the coefficient $b$ whose temperature variation is examined is not $b_m$, but the derived coefficient $b_{12}$, as defined in § 4. For it is this which connotes the action of unlike molecules upon one another in the mixture.

We have computed the various functions required for plotting the theoretical curves for a number of molecular models, in which the attractive index $m$ (equation (5)) was put at 5, and the repulsive index $n$ was put at 9, 10, 11, $14\frac{1}{4}$, 21, and $\infty$ respectively; in one other, $m = 6$, and $n = 11$. These curves, each with a different scale of abscissæ, were finally engraved on celluloid sheets, for the purpose of the comparisons which establish the right model, and for the parallel transformations that are needed to solve the equations for the force-constants. These comparisons were made with the experimental curve of log T against log $b$ (for pure gases) or log $b_{12}$ (for mixtures). The final results of this, which is a lengthy process, are given in the next section.

### § 8.

*Hydrogen.*—Repeating first of all Lennard-Jones's theoretical comparisons for this gas, and including all of Holborn and Otto's measurements, we obtain a qualitative correspondence with all of the models, and a fairly close match with the two models in which $n = 10$ and $n = 11$ ($m = 5$). For Holborn and Otto's data, Lennard-Jones found $n = 11$ preferable to $n = 9$ or $n = 14$. Within the temperature-range of 0° to 200°, we found $n = 10$ definitely better than the others ; our first five points were all on the curve, our two uppermost points being slightly low. The model with $n = 11$, $m = 5$, however, fits best if Holborn and Otto's low-temperature points ($b$ negative) are included.

*Helium.*—Lennard-Jones's comparisons (1924) gave for this gas the model $n = 14\frac{1}{3}$, $m = 5$, from compressibility data ; and this was in good agreement with a value $n = 14 \cdot 6$, obtained in Leiden for a non-attracting model from viscosity measurements. But Lennard-Jones used a blend of Onnes's data at low temperature with Holborn and Otto's from 0° to 400° ; and since that time, Holborn and Otto have published their further data at low temperatures (first to −183°, then to −258°) with results markedly differing from those of Onnes, but joining on very well with their own former curve.* Our own figures, as has been mentioned, lie closely between the other two sets and are in a temperature-range where these differ little from each other. In view of these later experiments, a revision of the helium model has been necessary. The result is to throw doubt upon the applicability of any one model when the entire range of Holborn and Otto's results is considered. Their figures at −258° and −252·8°, where $b$ is negative, do not fit the curves for any model which fits their other data from −208° upwards. The model $n = 14\frac{1}{3}$ represents only very roughly a loose general average of Leiden, Charlottenburg and our own figures. If, however, the comparisons are restricted to the range from −183° to + 400°, the model with $n = 11$, $m = 5$ fits very well ; and still better is $n = 10$, $m = 5$, which fits almost perfectly. For this range $14\frac{1}{3}$ is definitely not so suitable, and so also $n = 9$. The same remarks apply to our own data, whether considered by themselves or in conjunction with the others ; and to Onnes's data by themselves.

While the cause of the deviations below −250° remains obscure, the fact emerges that the molecular model best suited to the remaining isotherms is now brought within the same limits as had been found[†] most suitable for hydrogen, neon, argon, krypton, xenon, and nitrogen. No distance-index of repulsion higher than 11, nor one lower than 9, seems to be called for among these seven gases; and $n = 10$ is a fair average.

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* 'Z. Physik,' vol. 38, p. 359 (1926).

*Helium-Hydrogen.*—Using the values of $b_{12}$, calculated as shown in § 5 and tabulated in row iii of Table II, the theoretical comparisons show that the models with $n = 10$ and $n = 9$ are on the whole better than $n = 11$; $n = 14\frac{1}{3}$ is not very satisfactory.

The range of suitable models being thus defined, the force-constants, $\lambda$, appropriate to each model for each gas can be calculated, and they are shown in Table III.

Regarding the constants for the attractive component of force, it is seen

Table III.—Force-constants of $\lambda_m \,.\, r^{-m} - \lambda_n \,.\, r^{-n}$.

(Values got with the less suitable models are enclosed in brackets.)

| Model. | | Data used. | | 2He. | | 2H$_2$. | | He-H$_2$. | | He-H$_2$ calc. repul. $\lambda_n$. |
|---|---|---|---|---|---|---|---|---|---|---|
| $m$. | $n$. | | | Attract. $\lambda_m$. | Repul. $\lambda_n$. | Attract. $\lambda_m$. | Repul. $\lambda_n$. | Attract. $\lambda_m$. | Repul. $\lambda_n$. | |
| 5 | 9 | G. T. & M. | $10^{-44}\times$<br>$10^{-74}\times$ | (0·67) | (1·54) | 2·26 | 8·04 | 0·98 | 3·47 | (3·68) |
| | | L.-J.[*] | $10^{-44}\times$<br>$10^{-74}\times$ | 0·435 | 1·14 | 2·54 | 9·19 | | | |
| 5 | 10 | G. T. & M. | $10^{-44}\times$<br>$10^{-81}\times$ | 0·51 | 0·34 | 2·08 | 2·26 | 0·74 | 0·84 | 0·92 |
| | | H. & O. | $10^{-44}\times$<br>$10^{-81}\times$ | 0·46 | 0·33 | | | | | |
| 5 | 11 | G. T. & M. | $10^{-44}\times$<br>$10^{-89}\times$ | 0·405 | 0·75 | 1·66 | 6·06 | 0·57 | 2·02 | 1·97 |
| | | H. & O. | $10^{-44}\times$<br>$10^{-89}\times$ | 0·38 | 0·75 | | | | | |
| | | L.-J.[*] | $10^{-44}\times$<br>$10^{-89}\times$ | 0·291 | 0·62 | 1·98 | 7·38 | | | |

[*] Lennard-Jones's values for 2He were reckoned from Holborn and Otto's data between 0° and 400° only, combined with the data of Onnes between −216° and +100°. We show that the two sets of data are incompatible in the light of Holborn and Otto's new additional results between −258° and 0°, and we therefore include under 2He new readings of the whole of Holborn and Otto's data for helium, above −208°, together with the original readings of Lennard-Jones for the above models.

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[†] *Cf.* Lennard-Jones, 'Roy. Soc. Proc.,' A, vol. 112, pp. 227, 229 (1926).

that that between 2He is only about one-quarter of that between $2H_2$. That between He and $H_2$ is intermediate, and it is not very different from the value for 2He. A simple relationship is lacking.

Regarding the constants of the repulsive component, similar remarks apply. Here, however, Lennard-Jones has pointed out that the $(n-1)$th root of $\lambda_n$ for a mixture may plausibly be the arithmetic mean between the $(n-1)$th roots of the $\lambda_n$'s for the pure gases. The validity of this has been drastically tested here by calculating $(\lambda_n)_{12}$ accordingly from $(\lambda_n)_{He}$ and $(\lambda_n)_{H_2}$, and the results are seen in the last column of Table IV. Their concordance with the "observed" values is fair; the rule works well for the model $n = 11$.

### § 9.

The results of the analysis can now be put together so as to give a survey of the manner in which a pair of molecules of helium, or of hydrogen, or one of each kind, react together. Combining the attractive and the repulsive force-components, we get the nett intensity of intermolecular force at any specified distance apart; and the energy involved in the encounter is also calculable, and hence the "diameters," or distances of closest approach between molecules, can be found for each of the suitable models. For, if two molecules, acting upon each other according to equation (5), approach from infinity to a distance $r = \sigma$, the energy gained as a result of their encounter is given by

$$\frac{\lambda_m}{m-1} \cdot \frac{1}{\sigma^{m-1}} - \frac{\lambda_n}{n-1} \cdot \frac{1}{\sigma^{n-1}}. \tag{7}$$

Using in this expression the constants of Table III which have been found to hold for our gases, we find that it makes small difference in the results whether $n = 10$ or $n = 11$ (with $m = 5$), and the following account is true of either model.

At distances within about 10 to 15 Ångstrom units, these molecules begin significantly to attract each other, and thus to gain kinetic energy. As they close in upon one another, the nett intensity of attraction rises, and reaches a maximum in the neighbourhood of 4½ Å.; and then in the next Å. traversed, it rapidly falls off to zero. The gain in kinetic energy due to the whole encounter up to this point may be termed the "cohesion-energy." It is small, being less than 1 per cent. of the average K.E. of free thermal motion at 0° C. It is lost again when the next 0·5 Å. is traversed, for at this range (3 to 3½ Å.) the repulsive force-component has begun to predominate. The inter-molecular distance at this point is the closest approach of two molecules initially at rest and apart, moving together under the influence of their cohesive forces alone. If they are not initially at rest, but have been approaching with the K.E. of thermal translation as well as under their mutual influence, then they penetrate still further into each other's repulsive core. The extent of the further penetration in a direct encounter depends, naturally, upon the amount of thermal K.E. to be absorbed ; that is, with average molecules, upon the temperature of the gas. The higher the temperature, the closer the approach.

The distance of closest approach, which we shall term the kinetic diameter, can thus be specified for a pair of average molecules at any given temperature at which the same law of force holds, when once the force-constants have been found for these molecules. The following Table IV summarises the matter for our gases, for each of two models ; and at the foot of the table are some estimates from sources practically independent of the kinetic theory, which provide limits for comparison. Comparing the figures headed He-$H_2$ with

Table IV.—Cohesion-energies and Kinetic Diameters ($\sigma$).
(Energy in ergs ; distances in A.U.)

| | | Model $n = 10$, $m = 5$. | | | | Model $n = 11$, $m = 5$. | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 2He. | $2H_2$. | He-$H_2$. | $\frac{\sigma_{He} + \sigma_{H_2}}{2}$ | 2He. | $2H_2$. | He-$H_2$. | $\frac{\sigma_{He} + \sigma_{H_2}}{2}$ |
| $10^{15}$ × Cohesion-energy | | 0·39 | 1·08 | 0·38 | | 0·40 | 1·05 | 0·37 | |
| " Gained at $r$ = | | 3·67 | 4·05 | 4·08 | | 3·50 | 3·90 | 3·90 | |
| Lost at $r$ = | | 3·12 | 3·44 | 3·46 | | 3·01 | 3·37 | 3·35 | |
| K.E. corresponding to T° abs. lost at $\sigma$ :— | | | | | | | $\sigma$. | | |
| 0 | 0° | 3·12 | 3·44 | 3·46 | 3·33 | 3·01 | 3·37 | 3·35 | 3·19 |
| 4·12 × $10^{-16}$ | 1° | 2·98 | 3·38 | 3·31 | 3·18 | 2·89 | 3·31 | 3·20 | 3·10 |
| 41·2 | 10° | 2·58 | 3·07 | 2·85 | 2·82 | 2·55 | 3·02 | 2·82 | 2·88 |
| 412 | 100° | 2·10 | 2·55 | 2·32 | 2·32 | 2·09 | 2·55 | 2·31 | 2·32 |
| 823 | 200° | 1·95 | 2·39 | 2·16 | 2·17 | 1·96 | 2·40 | 2·17 | 2·18 |
| 1124 | 273° | 1·89 | 2·32 | 2·09 | 2·10 | 1·90 | 2·34 | 2·10 | 2·12 |
| 4116 | 1000° | 1·65 | 2·02 | 1·82 | 1·83 | 1·70 | 2·06 | 1·85 | 1·88 |
| Independent data :— | | | | | | | | | |
| Diameter of electric structure from dielectric constant* | | 1·20 | 1·84 | — | 1·52 | 1·20 | 1·84 | — | 1·52 |
| Upper limit of diameter from density of solid† | | — | 3·96 | — | — | — | 3·96 | — | — |

* From Jeans, 'Dynamical Theory of Gases,' 3rd ed., p. 333.

† *Ibid.*, p. 330.

those headed $\frac{1}{2}(\sigma_{He} + \sigma_{H_2})$, it appears that when a helium atom meets a hydrogen molecule, their joint kinetic diameter is practically the average of the respective kinetic diameters when each molecule meets its own kind. This additive relationship is seen to be most nearly true, as would be expected, for encounters which are energetic enough to bring the "harder" parts of the molecules into action. It is not unworthy of notice, though the point must not be stressed, that if the repulsive index can be taken as 10 for 2He and for $2H_2$, and 11 for He-$H_2$, the additive relation is almost exact for any encounter.

## *Experimental.*

### § 10.

Our methods ultimately consist in a series of comparisons of two volume ratios; one, for the gas under investigation; the other, for the manometric gas hydrogen, both being mounted in the same apparatus and subject to the same pressures. To the latter hydrogen volumes we then apply figures derived from the extremely precise and definitive work of Holborn and Otto on the compressibility of this gas, in order to learn what the pressures are. Thus our measurements of pressure are indirect, but they have the advantage of being referred to a substance at any time reproducible. Hydrogen, prepared with due care, is probably the best manometric gas; for, as far as is known, its compressibility is affected hardly at all by traces of its natural impurities, whereas other gases are more sensitive.

For various reasons we have used samples of gas measuring less than 10 c.c., and each sample has been examined over the whole range of pressures, so that our high-pressure volumes are as small as 80 cubic millimetres. With the procedure sketched below, we arrive at about ± 5 parts in ten thousand as the degree of reliability of the present *pv* data. This compares satisfactorily with other work in which much larger quantities of gas have been worked with. In Holborn and Otto's work, which appears to be the finest of its kind at the present time, from 1 to 11 litres of gas are compressed into a fixed volume of about 100 c.c., the pressure being measured with a hydraulic balance; and the divergencies usually found by them are about ± 1·5 to 2 parts in ten thousand.

The procedure may be briefly described under the headings: Preparation and purity of gases; measurements of samples; compression; calibration; and reduction of observations. Fig. 2 shows the essential apparatus used under the first two headings.

### *Preparation and Purity of Gases.*

### § 11.

*Hydrogen* was generated by electrolysing 30 per cent. KOH . Aq. to which barium hydroxide had been added to remove carbonates ; the electrodes were of nickel sheet, and the cell was a U-tube, kept cool in water. It was run for a day to remove dissolved air, and thereafter was not anywhere exposed to the atmosphere. From the cell (fig. 2, *b* 6), the gas passed over solid KOH and thence through electrically-heated palladium-asbestos (*a*, 6), and through $P_2O_5$, in order to remove the traces of oxygen inevitably present in such gas. It was then probably pure ; but to make sure, it was passed over the surface of a closed palladium tube, electrically heated to 350° (*a*, 1) ; and only that part of the gas which diffused through the solid palladium walls was collected in the gasholder. The whole system was thoroughly cleaned by evacuation and heating and by preparing a batch of diffused gas and then rejecting it. A batch of about 300 c.c. was then collected for use, the tap of the gasholder (*bc* 1) being thereafter kept sealed by mercury by means of the side-connections shown at *bc* 2. Successive batches, thus prepared, have given exactly concordant results when tested against one another in the compressor. Holborn's hydrogen was prepared by not dissimilar methods, and there is no reason to assume any difference in purity between the Charlottenburg hydrogen and our own.

*Helium* was made from a few litres stored over water, and had been drawn from a cylinder that had come from a Canadian works.* The gas was taken through a series of drying-tubes into gasholders over mercury, between which was a long U-tube filled with baked-out cocoanut charcoal and evacuated, and submerged in liquid air. To one gasholder was attached a density-bulb of about 300 c.c. coupled with a mercury manometer ; and the system was evacuated with a mercury-vapour pump. The crude gas contained about 10 per cent. of air. Manifold slow passages of the gas through the cooled charcoal left it with a density implying the presence of about 0·15 per cent. of air ; further repeated treatment brought the molecular weight to 4·01, and after further protracted "charcooling" the figure was 3·99. The accuracy of weighing the density-bulb gave a permissible variation of ± 0·01 units, hence the gas was now taken as pure. One of the gasholders containing it was fused to the main apparatus (*de*, 1), the tap being mercury-sealed. This furnished all of the helium used in the present work.

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* We owe thanks to Prof. F. G. Donnan, F.R.S., for the gift of this gas.

The foregoing details are recorded because of the slight differences between the data obtained for helium by Holborn and Otto, by the Leiden workers, and by us. Only two other gases might survive to any extent the charcoal treatment, which both Holborn and Otto and ourselves adopted; these are neon and hydrogen. The effect of either, if present as an impurity in helium, would be slightly to raise the value of the coefficient $b$ at ordinary temperatures. Holborn and Otto used a spectroscopic check to test the purity, we used the density; and it does not seem that the two modes of preparation could have led to any material differences in purity.

*Mercury* was purified for most of our work by A. S. Russell and Evans' method of shaking it with acidified ferric sulphate.*

### *Measurement of Samples.*

### § 12.

This was done near 15° C. and at pressures not exceeding 60 cm. The central features of the apparatus (fig. 2) are the multiple-point burette ($d$ 3), its barometer (4), and the compression-tube about to be filled ($bc$ 3). These formed part of a continuous glass system, other parts being the gasholders (1) and the barometric mercury reservoirs ($c$ 5, $e$ 5). The level of the mercury in the barometric system was controlled by changing the pressure of the dry air in the reservoirs, a capillary leak ($e$ 6) being provided for making fine adjustments. The temperature of the gas and of the barometric mercury was kept steady by a stream of thermostat-water which flowed through the vacuum-walled jacket of the burette, through the barometer-tank, and through the coils of small lead piping which enveloped the exposed mercury-leads ($e$ 3, 4).

Due precautions were taken for complete evacuation of the system; they were always tested by letting mercury rise through the burette until it reached the top of the capillary compression-tube. The residual gas never exceeded 0·00006 c.c. at 1 atmosphere. The experimental gas being then taken into the burette from the leads, its pressure and temperature were several times measured, with the mercury set at one of the burette-points. The barometer scale was read to 0·002 cm. with the micrometer eyepiece of a telescope. The measured gas was then pushed up completely into the vacuous compression-tube, and was followed by mercury. For mixtures, the second component was next measured in the same way, and was then passed up to join the first.

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* 'Chem. Soc. Trans.,' vol. 127, p. 2221 (1925).

component, and was followed by mercury into the bulb of the compression tube, with due precautions against the trapping of bubbles by the way.

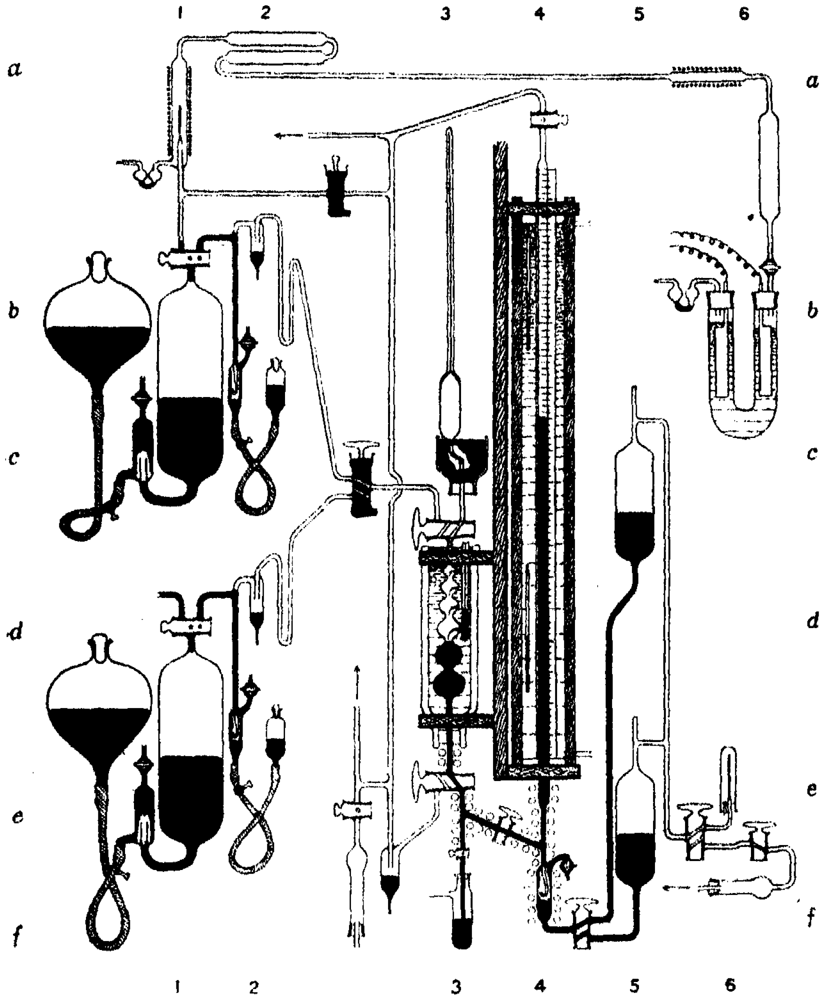

FIG. 2.

The constricted union between the burette and the compression-tube was now carefully snapped under the mercury of the seal (*c* 3) and with the aid of a small steel cup the whole compression-tube and its contents were removed to the compressor, with the lower end of the bulb submerged in the mercury with which that machine was filled.

### *Compression.*

### § 13.

The machine was one of those made for our earlier work, and its operation has already been described. The technique has been improved in numerous ways; we need only mention two of them here, namely the elimination of the "pressure-creep" by means of coils of lead-piping which controlled the temperature of the steel body of the compressor; and the comparison of only one gas tube at a time with the manometer tube, instead of three. For measurements at 25°, water from a thermostat flowed through the jackets of the tubes; for higher temperatures, the manometer tube was still kept at 25·00°, but the other gas tube was fitted with a wide jacket, in which heavy paraffin oil was heated by a nichrome resistance controlled by a regulator and was stirred by a stream of air-bubbles.

### *Calibrations.*

### § 14.

The volumes in the gas-burette, ranging from 2·5 c.c. to 25 c.c., were several times calibrated with mercury, using the calibration cock shown at *f* 3 in fig. 2. They were known to ± 1 in 30,000, excepting the smallest volume, for which the extreme uncertainty was ± 1 in 10,000. The pressures at each glass point in the burette, as recorded by the mercury-level in the barometric tube, were the subject of several separate investigations; for we find that the meniscus corrections given in the usual tables are not valid, at any rate when the mercury is dry and has been moving in tubes of diameter 0·4 and 1·0 cm. The meniscus-heights have been studied *in vacuo*, in contact with dry air, and with the experimental gases; and the registered pressures were eventually checked by using the burette for measuring the change of $pv$ of helium and also of hydrogen at pressures below 1 atmosphere. We find accordingly that an occasional error of a few parts in 10,000 in the measurement of a gas-sample has been possible. This would proportionately affect the coefficient $a$ in the resulting equation for $pv$, but it would leave the value of $b$ unaffected within the limits used in this paper.

The glass scales used with the compression-tubes were recalibrated in detail against N.P.L. standards.* The tubes used for the present work had a sectional area of 0·005 to 0·006 cm.$^2$; they were calibrated by the method of Isaac and Masson,[*] improved in detail. One of the tubes was now chosen as the standard, and a long set of interconnected comparisons was made by filling both it and each of the other tubes with pure hydrogen, and using the tubes to measure the apparent compressibility of this gas. By this means certain minor discrepancies in some of the original mercury calibrations were corrected; and in the whole of the work the volumes were thus reduced to one common standard. A large number of control experiments were made to arrive at reproducibility in the measurements.

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* We thank Prof. W. E. Curtis for the use of his Hilger travelling microscope for this purpose.

In connection with the compressions at higher temperatures, additional calibrations of the tubes, with mercury, were made at 100° and at 175°; and the expansion-coefficients thus obtained were applied to all the high-temperature observations.

The thermometers were standardised by us in ice, in steam, and against thermometers bearing N.P.L. certificates.

### *Reduction of Observations.*

### § 15.

The units to which all the observations were reduced are :—

*Pressures* :—

In International Atmospheres, *i.e.*, 1 int. atm. = pressure of 76·000 cm. of mercury at 0° and with $g = 980 \cdot 665$.

*Volumes* :—

For pure gases,

$$v = \frac{\text{cubic centimetres of gas at } p \text{ and at } t^\circ \text{ C.}}{\text{cubic centimetres of same gas at 1 atmosphere and } 0^\circ \text{ C.}}\,\dagger$$

For mixtures,

$$v = \frac{\text{cubic centimetres of mixed gas at } p \text{ and at } t^\circ \text{ C.}}{\text{sum of separate volumes at 1 atmosphere and } 0^\circ \text{ C.}}$$

The reductions of the measurements made in filling the tubes call for no special remark. The observations in the compressions are treated thus :—

From the observed length of gas-column, up to the foot of the meniscus in the capillary tube, is subtracted a small correction, equal to about one-half the height of the meniscus, derived from the data of Schalkwijk.[*] The resulting length, when the calibration-table for the tube is applied, gives the volume. From a value of $v$ at 25·00° for the manometric hydrogen tube, the pressure is found from tables drawn up for the equation :

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[*] 'J. Phys. Chem.,' vol. 28, p. 166 (1924).

[†] Note that in the earlier paper, for the purpose there in view, $v$ was referred to 1 atmosphere and $t^\circ$ C. Neglect of this fact led Crommelin and Watts ('Comm. Phys. Lab. Leiden,' No. 186c (1928)) to criticise destructively our results with ethylene, but, as Dr. Crommelin has kindly acknowledged in correspondence, the criticism is entirely based upon an error on the part of these authors.

$$pv = 1\cdot090850 + 0\cdot0_3 6592p + 0\cdot0_7 723p^2.$$

This was interpolated graphically from Holborn and Otto's similar equations for their data at 0°, 50°, and 100° for hydrogen, their units being first converted into ours. To the manometer-pressure so found, a correction is added to allow for any differences in the head of mercury in the gas-tube as compared with the manometer tube ; and the result is the pressure of the gas, $p$. A better interpolation, using these authors' later values at additional temperatures, has given us $0\cdot0_3 656$ for $b$ and $0\cdot0_6 105$ for $c$. It can readily be shown, however, that for manometric purposes the two equations differ by less than one part in 10,000, and the error has thus been negligible for our present purpose. But it ought to be noted that the use of the later value of $b$ for hydrogen would considerably lessen the apparent irregularity at the corresponding part of fig. 1, making clearer the enhancement of $b$ due to admixture with helium ; and it would also slightly improve the agreement between " observed " and " calculated " values in Table I. These changes are near the experimental limit. In applying the manometric equation to pressures beyond 100 atmospheres we have gone outside the data on which it is based ; but as far as can be judged from our present experiments, the extrapolation to 125 atmospheres has not led to any material error.

The fluctuations in temperature between the manometer and the gas at 25° were hardly ever as great as 1 in 10,000, and usually only about one-third of this. Where necessary, corrections were applied. With the gas at high temperatures, variations up to a few tenths of a degree occurred ; the resulting figures at each pressure-reading were corrected accordingly to the average temperature of the run.

The values of $pv$ were plotted against $p$ from about 30 atmospheres upwards on a wide scale, in which 1 mm. $= 0\cdot0002$ units of $pv$ and 1 mm. $= 0\cdot2$ atmosphere. For all of our gases the resulting curves could be taken as straight lines. In finding the correct straight line with the aid of a thread stretched along the 10 to 20 points of a given series, we have found the simple criterion of Dufton[†] a most useful preliminary guide, and with our experiments this criterion left practically no room for arbitrary choice in the slope of the curve.

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[*] 'Comm. Phys. Lab. Leiden,' No. 67 (1901).

[†] 'Nature,' vol. 121, p. 866 (1928) ; *cf.* also de Bray, *ibid.*, vol. 122, p. 171 (1928).

It will be noted that in the graphical method, the values of the coefficient *a* are found by extrapolation, and so they carry in them any errors of the kind mentioned in § 14 to which the burette-measurements were liable. The value of *a* should not be expected to be constant for the mixtures; according to their deviations from Dalton's law, it should increase from 1·09085 for either pure gas up to a maximum of about 1·0913 in a 50 : 50 mixture. Table V should be examined with these two remarks in mind.

The experimental results are too numerous to be printed in detail, but

Table V.

| Temperature. | Series. | Per cent. He. | $pv = a + bp$. | | Number of points. | Mean error in $pv$. |
|---|---|---|---|---|---|---|
| | | | $a$. | $10^4 b$. | | |
| 25·00° ± 0·02 | 1 | 100·00 | 1·09085 | 5·10 | 11 | 0·00046 |
| | 17 | 100·00 | 1·09085 | 5·10 | 12 | 22 |
| | 6 | 83·49 | 1·0912 | 5·67 | 10 | 63 |
| | 8 | 73·99 | 1·0909 | 5·92 | 20 | 47 |
| | 3 | 66·64 | 1·0904 | 5·97 | 11 | 43 |
| | 7 | 57·54 | 1·0911 | 6·36 | 15 | 38 |
| | 24 | 50·11 | 1·0916 | 6·38 | 12 | 22 |
| | 4 | 50·06 | 1·0915 | 6·41 | 10 | 53 |
| | 10 | 42·42 | 1·0915 | 6·56 | 12 | 33 |
| | 2 | 33·00 | 1·0901 | 6·62 | 11 | 45 |
| | 9 | 26·40 | 1·0904 | 6·61 | 20 | 49 |
| | 5 | 16·26 | 1·0905 | 6·56 | 10 | 29 |
| | (H & O) | 0 | 1·09085 | 6·560 | $(+1·05 . 10^{-7}p^2)$ | — |
| 50·0° ± 0·1 | 18 | 100·00 | 1·1827 | 5·07 | 12 | 39 |
| | 25 | 50·11 | 1·1836 | 6·44 | 12 | 48 |
| | 12 | 0·00 | 1·1832 | 6·71 | 12 | 55 |
| 75·0° ± 0·1 | 19 | 100·00 | 1·2748 | 5·02 | 12 | 39 |
| | 26 | 50·11 | 1·2751 | 6·37 | 12 (11) | 83 (69) |
| | 13 | 0 | 1·2748 | 6·86 | 12 | 45 |
| 100·38° ± 0·1 | 20 | 100·00 | 1·3669 | 4·86 | 11 | 67 |
| | 27 | 50·11 | 1·3676 | 6·43 | 12 | 53 |
| | 11 | 0·00 | 1·3669 | 6·93 | 12 | 46 |
| 125·2° ± 0·2 | 21 | 100·00 | 1·4605 | 4·94 | 12 | 58 |
| | 28 | 50·11 | 1·4592 | 6·20 | 12 | 43 |
| | 14 | 0·00 | 1·4582 | 7·02 | 12 | 43 |
| 150·1° ± 0·2 | 22 | 100·00 | 1·5486 | 4·62 | 12 | 122 |
| | 29 | 50·11 | 1·5494 | 6·41 | 12 | 74 |
| | 15 | 0·00 | 1·5516 | 6·93 | 18 | 124 |
| 175·0° ± 0·3 | 23 | 100·00 | 1·6357 | 4·87 | 11 | 93 |
| | 30 | 50·11 | 1·6455 | 6·20 | 12 | 70 |
| | 16 | 0·00 | 1·6420 | 6·87 | 11 | 61 |

Table V gives an epitome, showing for each series: the constants $a$ and $b$ in the equation (1) used to express the values of $pv$ measured in that series; the number of points at which $p$ and $pv$ were measured, these being spread evenly over the range 30 to 125 atmospheres; and the arithmetic mean of the deviations of the experimental values for $pv$ from those calculated with the equation.

## *Summary.*

(i) Continuing former work with other gases, we have measured the compressibilities, up to 125 atmospheres, of helium, hydrogen, and 10 mixtures of the two at 25°; and those of both pure gases and an equimolecular mixture at 7 temperatures from 25° to 175°. The experiments are described.

(ii) The deviations from Dalton's law of partial pressures are positive, and are at a maximum in an equimolecular mixture, where, under high compression, they attain 4 per cent. of the ideally additive pressure.

(iii) Within a certain range of compositions, mixtures of these two gases are still more incompressible than hydrogen.

(iv) The data are expressible by equations $pv = a + bp$ within the experimental limits of $\pm$ 5 in 10,000; the values of $a$ and $b$ for each gas and each temperature are recorded.

(v) The influence of gas-composition upon the values of $b$ for the mixtures is studied; and, by means of the partial pressure equation of Lennard-Jones, the facts are shown to support the assumption that a spherically symmetrical field of force surrounds a helium molecule, and a hydrogen molecule.

(vi) The influence of temperature upon the values of $b$ for the pure gases and the mixture is examined, in the light of Lennard-Jones's analysis of intermolecular forces. The results accord with his theory of superposed forces of attraction and repulsion around each molecular centre in an encounter. The distance-indices of these forces are evaluated for encounters between 2He, between $2H_2$, and between He and $H_2$. With a distance-index of $-5$ for the attractive component, the index for the repulsive component is found to be $-10$ or $-11$ in all three cases. For pure hydrogen and pure helium, the data of other workers, and the values already calculated from them by Lennard-Jones, are reviewed in conjunction with our own.

(vii) The force-constants are evaluated; and it is found that the constants for an encounter of He with $H_2$ are considerably nearer to those for 2He than to those for $2H_2$.

(viii) The energy-factors of these three types of molecular encounter are calculated from the constants of (vi) and (vii). For each, the cohesion-energy

is defined and is tabulated, together with the kinetic diameters appropriate to various temperatures. The intermolecular distances of closest contact between He and $H_2$ approximate to the sum of the two kinetic half-diameters.

It is a pleasure to acknowledge the help of a grant which was made by the Council of the Department of Scientific and Industrial Research in connection with this work; and to acknowledge a grant from the Chemical Society which defrayed some of the expenses.

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# *Some Experiments Concerning the Counting of Scintillations Produced by Alpha Particles.—Part* I.

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## INTRODUCTION.

Among the various methods of detecting single α-particles, the scintillation method, because of its simplicity, is often the only one applicable. When the particles are to be counted in the presence of a strong β and γ radiation, the scintillation method is indispensable, for the scintillations produced by α-particles are easily detectable on the luminous background produced by the β and γ rays, while the electrical counter is seriously disturbed by these types of radiation.

Though the counting of scintillations has been constantly used as an experimental method since 1908, and practically all the fundamental data on which the modern conception of atomic structure is based, were obtained by this method, very little systematic work has been done concerning the method itself and its limitations.

The object of this work was to investigate in detail all the factors involved in the method of scintillation counting, and to connect the various isolated pieces of information which have been given from time to time by the workers in this field.

In order to obtain a clear picture of the process of scintillation counting, it was desirable to examine separately each link of the chain of phenomena involved. Some of the phenomena indeed are of individual interest.

The two fundamental processes involved are :—

(1) The transformation of the energy of the α-particle striking the zinc-sulphide screen into radiant energy ; and

(2) The detection of this radiant energy by the eye under various conditions of observation.

The following experiments were accordingly undertaken :—

(1) The determination of the smallest amount of luminous energy perceptible by the eye.

(2) The measurement of the efficiency of the transformation of the kinetic energy of the α-particle into radiant energy.

(3) The determination of the velocity of the slowest α-particles detectable by the scintillations they produce.

(4) The investigation of the influence of the numerical aperture of the microscope employed on the results of counting.

These experiments will be described in this paper and their connection with one another discussed.

In the course of the paper, several technical expressions are used which are perhaps somewhat unfamiliar to the general reader. For convenience, definitions of these terms are given here.

### *Definitions.*

(1) *The lumen* is the unit of luminous flux, being the flux radiated in unit solid angle by a source of one candle-power.

(2) *The luminosity* of a monochromatic light is the ratio of the sensitivity of the eye to this light, to the sensitivity of the eye to light of wave-length 0·53 μ for which the eye is most sensitive under normal conditions.

(3) *The scotopic luminosity* is defined similarly for the dark adapted eye which is most sensitive to the light of wave-length 0·505 μ.

(4) *The mechanical equivalent of light* is the ratio of the radiant flux to luminous flux for the wave-length of maximum luminosity, and is expressed in watts per lumen. The most reliable determination was made by Ives who gives the value 0·0016 watts per lumen.

(5) *The energy radiated by a given source of light evaluated as green light*, is the energy radiated by a source emitting light of that wave-length for which the eye is most sensitive, and appearing of the same brightness as the given

source. If $E_\lambda$ is the intensity of the radiation from the source under consideration, at the wave-length $\lambda$, then the energy radiated from the source evaluated as green light will be

$$\int_0 E_\lambda \times \text{luminosity}\,\lambda\, d\lambda.$$

### *The Determination of the Smallest Amount of Luminous Energy Perceptible by the Eye.*

For the present purpose of investigating the method of scintillation counting, we are interested, not so much in the general question of the sensitivity of the dark adapted eye, as in its sensitivity under conditions similar to those under which scintillations are counted, that is to flashes of short duration.

According to Wood* and Wertenstein,† the duration of a scintillation is about $10^{-4}$ seconds. The only measurements which have been made on the sensitivity of the eye to such flashes appear to be those of Grijns and Noyons.‡ They determined the sensitivity of the eye for short flashes of various durations, and found that the energy necessary to produce a visual sensation depended on the time during which the energy was supplied to the eye. The smallest amount of energy was perceived when supplied in flashes of $5 \,.\, 10^{-3}$ seconds, and the value of this minimum energy was $4 \,.\, 10^{-11}$ erg (10 quanta, $\lambda = 0 \cdot 505\mu$). The results obtained by these authors cannot, however, be considered reliable. An analysis of their work reveals errors not only in the general calculations, but, owing to a misinterpretation of the geometrical conditions of their experiments, also in the estimation of the energy entering the eye in the shorter flashes.

The sensitivity of the eye for very short flashes of light has been investigated by Poole,§ who produced flashes lasting only about $10^{-7}$ seconds by means of a rapidly rotating mirror. He found for the minimum energy perceptible a value of about $4 \,.\, 10^{-7}$ erg (10,000 quanta, $\lambda = 0 \cdot 505\ \mu$). The conditions do not correspond to those holding in the counting of scintillations, and it is clear from a variety of evidence that, for flashes of about the duration of a scintillation, a much smaller amount of energy than the above can be perceived.

A certain amount of data exists on the sensitivity of the eye for steady light, some of which may be mentioned here. For example, Russell[*] has determined the smallest amount of radiation visually perceptible by observing white discs illuminated by the steady light of a star. The values obtained, calculated in terms of the wave-length for which the eye is most sensitive, were $7 \,.\, 10^{-10}$ erg per second (170 quanta per second, $\lambda = 0 \cdot 505\ \mu$).

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* 'Phil. Mag.,' vol. 10, p. 427 (1905).

† 'J. Physique,' vol. 2, p. 21 (1921).

‡ 'Archiv Physiol.,' p. 25 (1905).

§ 'Phil. Mag.,' vol. 43, p. 345 (1922).

Similar measurements were made by Buisson[†] who observed the fluorescence of zinc-sulphide screens under the action of a radioactive source. He obtained values varing from $11 \,.\, 10^{-10}$ to $15 \,.\, 10^{-10}$ erg per second.

It is not without point to refer here to the experiments of Reeves[‡] on the effect of the size and shape of the stimulus on the minimum radiation perceptible, for they show clearly that the size of the retinal image plays an important rôle in all such determinations. For example, the value obtained for the limit, when the stimulus was a circle of 1 mm. diameter, placed at a distance of 3 metres from the eye, was $17 \cdot 1 \,.\, 10^{-10}$ erg per second, while a square of 12 mm. side placed at a distance of 35 cm. from the eye gave the value $564 \,.\, 10^{-10}$ erg per second.

From these values for steady light, it is possible to draw some conclusions about the sensitivity of the eye to short flashes. As the period of relaxation of the eye is of the order of 0·1 second, the amount of energy which must be supplied to the eye per second in order to produce the sensation of steady light should be about 10 times more than the energy required to produce the sensation of a short flash of equal intensity. This cannot, however, be accepted without experimental proof, and a new determination seemed desirable, especially in view of the high values obtained by Poole[§] for the minimum energy perceptible when supplied to the eye in very short flashes.

In the experiments described below, the conditions under which scintillations are observed were imitated as closely as possible. The duration of the flash could be varied within wide limits, namely, from 0·1 second to $5 \,.\, 10^{-5}$ seconds, and the colour of the light was adjusted to correspond with that of a scintillation. A telescope was used for the observation of the flash so that the eye could be relaxed as in the counting of scintillations with a microscope. In order to make the results as definite as possible, the source of light was made of such a size that the image formed on the retina had the dimensions of the order of a single retinal cell. Thus a further decrease in the size of the source should not affect the results unless there is some kind of ultramicroscopic structure to the cell itself, which does not seem probable.

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[*] 'Astrophys. J.,' vol. 45, p. 60 (1917).

[†] 'Astrophys. J.,' vol. 46, p. 296 (1917).

[‡] 'Astrophys. J.,' vol. 46, p. 167 (1917), and vol. 47, p. 141 (1918).

[§] *Loc. cit.*

The description of the arrangement designed to fulfil these conditions follows.

### *Description of Apparatus.*

A small hole (see fig. 1) in the wall of a box B, in which a gas-filled lamp L was placed, was used as a source of light.

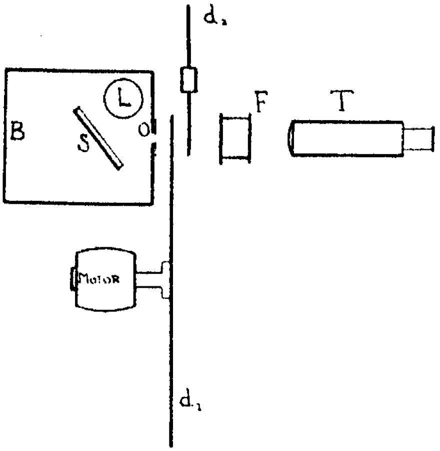

FIG. 1.

A system of two rotating discs $d_1$ and $d_2$ provided with slits exposed the hole once every second and permitted the duration of the flash to be varied at will from 0·1 to 5 . $10^{-5}$ seconds. The light escaping from O passed through a filter F and was observed by means of a telescope T. The quantity of light entering the telescope during a flash of definite duration could be varied by placing diaphragms of various diameters over the objective. Geometrical conditions were so arranged that the quantity of light entering the telescope at any instant of a flash increased to its maximum value and diminished again in a time as small as possible compared with the time at which it was maintained at its maximum value.

### *The Source of Light.*

The beam of light escaping from the hole O forms an inverted image of the inside of the box. It is obvious therefore that the direct illumination of the hole by the incandescent filament is impossible if a uniform beam be desired. Various methods of obtaining a sufficiently strong uniform beam of light were tried, and it was found that the best results were obtained by illuminating the hole by light diffused from a magnesium oxide screen S (fig. 1). This screen was prepared by holding a copper plate above a burning magnesium strip; and was placed about 10 cm. from the hole and illuminated by a lamp L standardised at the National Physical Laboratory (70 c.p. colour temperature* 2660° K.).

### *Flash Production.*

The duration of the flash was regulated by the wheel $d_1$ of 80 cm. diameter made of stout cardboard. A hole was cut in the wheel near the periphery so that it passed in front of the hole O during the rotation. This hole could be covered by cardboard in which slits of various widths were made. In order to avoid excessive vibrations at rapid rotation a similar hole was cut in the opposite end of the same diameter and covered with thin cardboard.

The wheel was fixed to the shaft of an electric motor which ran at 600 r.p.m. The distance from the hole O to the centre of the shaft was 36·8 cm. The duration of a flash was therefore $4{\cdot}33 \,.\, 10^{-4} \,.\, s$ seconds where $s$ cm. was the width of the slit.

If the wheel $d_1$ alone had been used the luminous point would have been exposed 10 times per second, thus producing an undesirable summation effect since the sensation in the eye lasts longer than one-tenth of a second. To obviate this effect and also to make the flashes follow each other after convenient intervals of time, a second wheel $d_2$ was used which was rotated at 60 r.p.m. by means of a reducing gear and a small electric motor. In this way only one out of every 10 flashes made by the large wheel $d_1$ was observable when both wheels were rotating. Synchronism was easily maintained—only one from about 100 flashes being missed. The possibility of two exposures occurring during one passing of the selection sector was eliminated as its length was less than one-tenth of the circumference.

The telescope consisted of four lenses, the original stop being of 4 cm. diameter. It was placed at a distance of 154 cm. from O.

### *Dimensions of Luminous Point.*

As has been already stated, it was desirable that the retinal image of the luminous point should be of the same dimensions as the retinal cells. The hole was made in thin metal foil with a very fine needle, and examination under a microscope showed that its shape was a very good circle of 30 $\mu$ diameter. The magnification of the telescope was 16 and its distance from the hole was

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* See *e.g.*, Walsh, 'Photometry' (Constable & Co., London), p. 270 (1926).

154 cm. The diameter of the retinal image was therefore $6 \,.\, 10^{-4}$ cm., the focal length of the eye being taken as 2·2 cm. The diameter of a retinal cell is of the order of $5 \,.\, 10^{-4}$ cm.* for peripheral vision.

### *The Filter and Focussing Screen.*

The filter used consisted of a glass vessel with parallel walls containing an aqueous solution of copper sulphate and potassium chromate. Several drops of ammonia were added to prevent precipitation.

The composition was chosen in such a way that the minimum of absorption was near the wave-length 500 $\mu\mu$. The band of transmitted light was contained approximately between the limits 470 to 520 $\mu\mu$. The method of measurement of the transmission curve of the filter will be described later.

In front of the filter and the rotating discs a white cardboard screen was placed with a hole (about 5 mm. diameter) cut in it through which the luminous point was observed. This screen was illuminated with a faint red light, which does not appear to hinder the process of dark adaptation appreciably. This screen was used to facilitate the focussing of the eye which was very difficult, if not impossible, if there was nothing but the flashing point at which to look. The field of view therefore consisted of a faintly illuminated ground, in the middle of which was a dark circle, the flashing point appearing in the centre of this dark circle.

### *Experimental Procedure.*

The experiment consisted of four parts :—

(*a*) Determination of the intensity of the beam of light escaping from O.
(*b*) Determination of the transmission curve of the filter.
(*c*) Determination of the quantity of light lost in the telescope.
(*d*) Determination of the conditions (slit width and telescope stop) corresponding to the "limit."

(*a*) *Intensity of the Beam from* O.—Part of a photographic plate covered by an optical wedge was exposed to the direct light from the lamp L. (The lamp L was placed in a special blackened box with suitable diaphragms to prevent scattered or reflected light reaching the photographic plate.) The lamp was then placed in its proper position in the box, and the remaining part of the photographic plate exposed directly to the light escaping from the hole O. The distances of the photographic plate from the sources of light were chosen in such a way that the blackening produced in the photographic plate by the light from the hole O was intermediate to the blackenings produced by the lamp and the optical wedge, the exposures being equal in both cases. The blackening of the photographic plate directly illuminated by the lamp was plotted against the reduction factor of the wedge. From this curve the value of the reduction factor could be obtained which would have produced a blackening equal to that produced by the hole O. This reduction factor which was the ratio of the illuminations of the two plates was found to be 3885. The distance from the lamp to the photographic plate was 390 cm. while that from the hole to the plate was 3·9 cm., and therefore since the candle-power of the lamp was 70 c.p. the candle-power of the hole O was $1 \cdot 8 \,.\, 10^{-6}$ c.p., and the colour temperature of the hole being the same as that of the lamp was 2660° K.

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* Walsh, *loc. cit.*, p. 21.

Now the power radiated in unit solid angle by a source of colour temperature T may be written $\int_0^\infty E_\lambda \, d\lambda$ watts, where $E_\lambda = C_1 \lambda^{-5} e^{-C_2/\lambda T}$, where $C_2 = 14350$, $\lambda$ being measured in microns, and an evaluation of the integral for a source of colour temperature 2660° K. gives

$$\frac{6C_1}{853}.$$

$C_1$ can be determined graphically with the help of the equation

$$C_1 \int_0^\infty \frac{E_\lambda}{C_1} \times \text{luminosity}\,\lambda \, d\lambda = \text{candle-power} \times \text{mechanical equivalent of light.}$$

If the values of $E_\lambda/C_1 \times$ luminosity $\lambda$ are plotted as a function of $\lambda$, then taking as units microns and degrees, we obtain for the value of the area under the curve $1 \cdot 24 \,.\, 10^{-4}$. Hence, taking 0·0016 as the value of the mechanical equivalent of light in watts per lumen, we have for the value of $C_1$, $2 \cdot 31 \,.\, 10^{-5}$ for a source of colour temperature 2660° K., and candle-power $1 \cdot 80 \,.\, 10^{-6}$. Hence the power radiated in unit solid angle from the hole O was $1 \cdot 62 \,.\, 10^{-7}$ watts.

*The Transmission Curve of the Filter* was determined by means of a spectrograph. The same lamp was used as a source of light, one spectrum being taken with the filter in front of the collimator slit, and several others of the same duration with the filter removed and the various steps of an optical wedge in front of the slit. The wedge was a photographic plate, successive strips of which had been exposed to uniform illumination for increasing times. The plate was developed and the absorption factors of the various steps measured with a microphotometer.

On microphotometring the spectra obtained in this way, a curve was obtained for the light transmitted by the filter with a series of other curves* intersecting it (fig. 2)—one for each step of the optical wedge. At the wave-lengths, then, corresponding to the points of intersection of the series of curves with the filter curve, the absorption of the filter was equal to the absorption factor of the wedge step which produced the intersecting curve. In this way a transmission curve of the filter could be plotted which was independent of the properties of the photographic plates used.

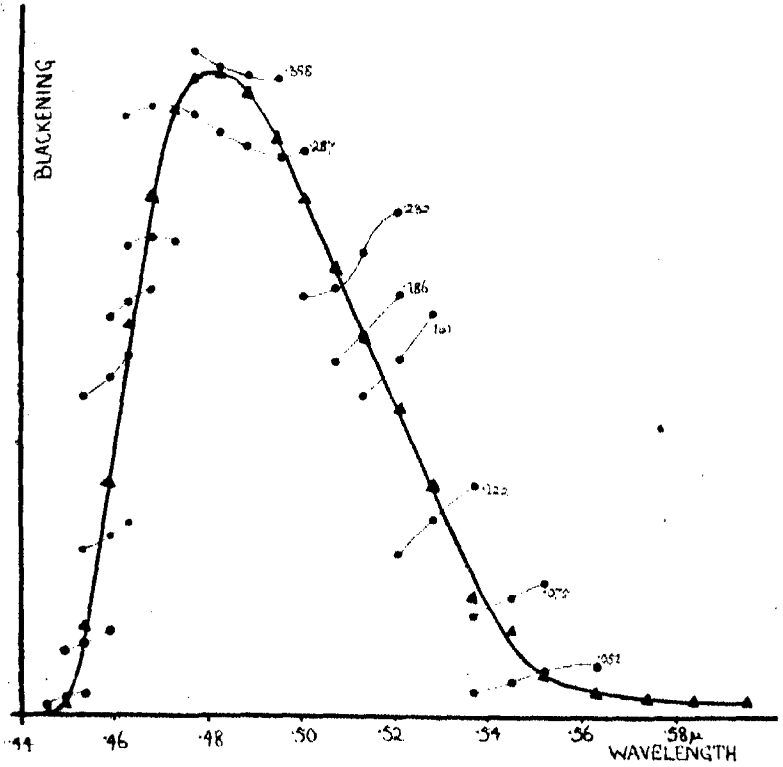

FIG. 2.

▲ Spectra taken through filter.
● Spectra taken through optical wedge.

The figures give the transmissivity of the wedge.

The fraction of the energy in a beam of light of colour temperature 2660° K. falling on the filter which would be transmitted was calculated graphically.

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* Only those parts of the members of the series of intersecting curves near the points of intersection were actually microphotometered.

A curve was plotted (see fig. 3) giving the product of the intensity $E_\lambda$ in a source of colour temperature 2660° abs. and the transmission factor $t_\lambda$ of the filter for the same wave-length against the wave-length.

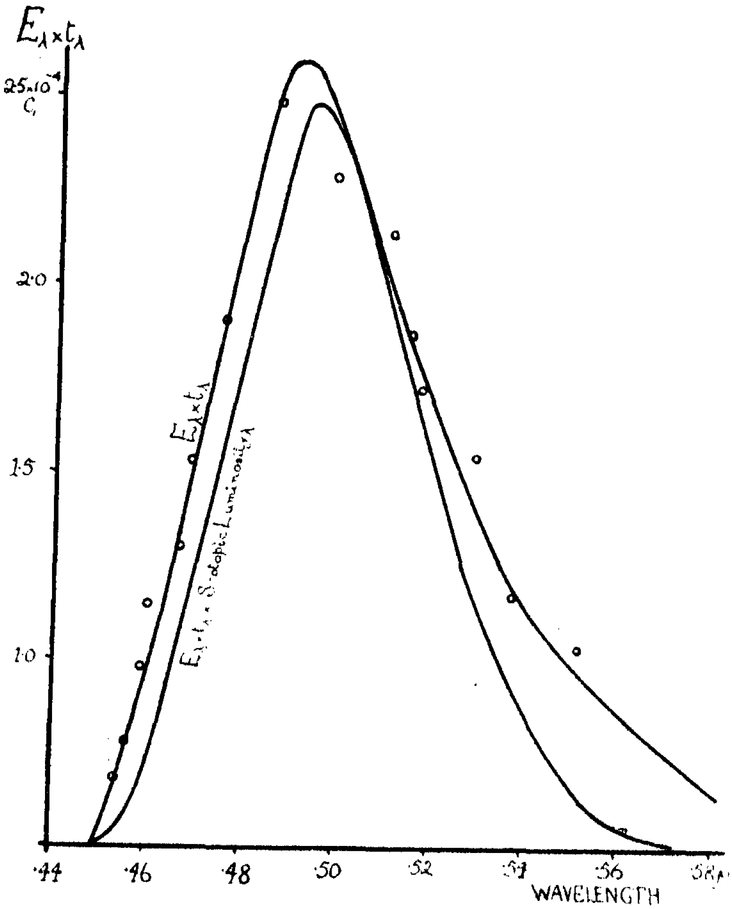

FIG. 3.

The area under the $E_\lambda t_\lambda$ curve using microns and degrees as units was found to be $1 \cdot 26\, C_1 . 10^{-5}$.

The area under the $E_\lambda$ curve has already been seen to be $6C_1/853$. The ratio of these two areas gave the fraction of the energy transmitted by the filter; or the transmissivity of the filter was $1 \cdot 8 . 10^{-3}$. Multiplying the power radiated from the hole O by this transmissivity, we obtain for the power radiated in unit solid angle through the filter, $2 \cdot 92 . 10^{-3}$ ergs per second. This value gives the actual number of ergs per second in the beam of light passing through the filter. The energy radiated by the filter is distributed over a considerable portion of the visible spectrum. The eye, therefore, is not equally sensitive to all the energy in the beam. The energy in a beam of wave-length for which the dark adapted eye is most sensitive, which would be of the same brightness as that passing through the filter can be found by taking, as the transmissivity of the filter the ratio of the area under the $E_\lambda t_\lambda$ $\times$ scotopic luminosity curve to that under the $E_\lambda$ curve. The scotopic luminosity $\lambda$ is given by the curve of bleaching of the visual purple.* The curve $E_\lambda t_\lambda \times$ scotopic luminosity $\lambda$ is plotted also in fig. 3; the area under it is found to be $0 \cdot 96 \,.\, 10^{-5}$ $C_1$, thus the transmissivity becomes $1 \cdot 4 \,.\, 10^{-3}$. This gives for the power radiated through the filter in unit solid angle $2 \cdot 3 \,.\, 10^{-3}$ ergs per second, evaluated as green light ($\lambda = 0 \cdot 505\ \mu$).

It must be noted here that the light emitted from the hole could have been evaluated as green light with the help of the scotopic luminosity curve without the use of the filter. The filter was used, however, to reduce the possible error introduced by using the bleaching curve of the visual purple as a true scotopic luminosity curve.

(*c*) To determine the fraction of the light lost in passing through the telescope the following method was used. The upper part of the screen P (fig. 4) was directly illuminated by a source of diffused light S, which consisted of a piece of ground glass fixed to the end of a short brass tube containing a small electric lamp *l*. On the lower portion of the screen, the image of the source of light was formed by the telescope T. The distances were adjusted until the brightness of this image was equal to the brightness of the screen illuminated directly by the source of light. The adjustment was checked by replacing the screen P by a photographic plate, and measuring the blackenings of the plate microphotometrically. The transmissivity of the telescope could then

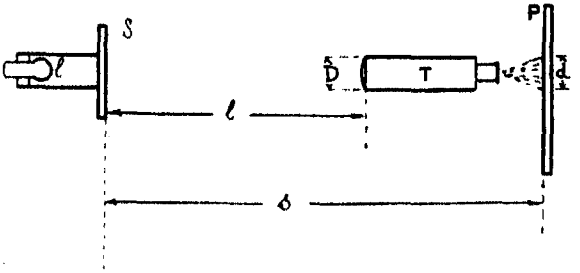

FIG. 4.

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* Walsh, *loc. cit.*, p. 73.

be calculated from the distances involved and the ratio of the areas of the object glass of the telescope and the image of the source of light. The value obtained for the transmissivity was $0 \cdot 575$.

### *Evaluation of the Energy entering the Eye in a given Flash.*

We have seen that the power radiated in unit solid angle through the filter was $2 \cdot 27 . 10^{-3}$ ergs per second, and since the distance of the telescope from the hole O was 154 cm. and the transmissivity of the telescope was $0 \cdot 575$, the power entering the eye per square centimetre of aperture of the telescope was $5 \cdot 5 . 10^{-8}$ ergs per second. The duration of a flash being $4 \cdot 33\ s . 10^{-4}$ seconds where $s$, the width of the slit in the wheel $d_1$, is measured in centimetres, the energy entering the eye in a flash was $2 \cdot 38 \times a \times s \times 10^{-11}$ ergs, where $a$ is the area in square centimetres of the telescope aperture used.

In order to assist the visualisation of these small fractions of an erg, they will be expressed in the sequel in number of quanta, taking for the value of the quantum $3 \cdot 9 . 10^{-12}$ ergs ($\lambda = 0 \cdot 505\ \mu$). Hence the energy in a flash, given above, will be written as $6 \cdot 1 \times a \times s$ quanta.

(*d*) *Determination of the Slit Width and Aperture Corresponding to the Limit.*—While observing the faint, regularly occurring, point flashes it was noticed that the eye became fatigued very quickly. Whether the fatigue was retinal, muscular, or psychological it was difficult to decide. When the flashes were only just visible it was noticed, that though the first few flashes were quite definitely observable immediately after placing the eye at the telescope, only occasional ones could be detected later ; after resting the eye for half a minute or so by glancing about the darkened room, the first few flashes were again observable, followed only by occasional ones. This led to the following method of estimation of the " limit." An observer on placing his eye in position counted the number of consecutive flashes (maximum 3) which he was able to see. If he was unable to see any before the end of an estimated 20 seconds, or so, the number observed was said to be zero. Five trials were made by each observer for any given intensity of flash and the percentage observed out of a possible 15 tabulated. For any given duration of flash an observer made five such trials for each of a number of telescope apertures. The percentage of the possible 15 flashes observed in each trial was plotted against the intensity of the flash, and the curve so obtained extrapolated to the axis of abscissæ, giving an estimate of the " limit " visible. This definition of the " limit " contains a large element of arbitrariness, caused in part by the possibility of probability fluctuations in the small number of quanta forming a flash. It was noticed, however, that if any of the flashes of a given intensity were detected by an experienced observer then he was able to detect over 90 per cent. of the flashes of double the intensity. Every precaution was taken to prevent an observer obtaining any information as to the brightness of the flashes he was observing. The illumination of the focussing screen and the aperture of the telescope were altered without rule while the observer was resting his eyes.

The points plotted formed a regular curve only when the observer had had good experience of scintillation counting. A series of trials were made by each of three experienced counters, and it was only in these cases that the curves could be reasonably extrapolated.

Fig. 5 shows the results obtained, for the same duration of flash, by an experienced and an inexperienced observer. It will be seen that the curve plotted for the number of flashes observed against the energy in the flash falls off much more abruptly for an experienced than for an inexperienced observer. Two reasons can be held to account for this effect. Experience increased the number of consecutive flashes observed when the energy in the flash was large, for it facilitated concentration and enabled the eye to be consciously moved about the field of view, thus seemingly preventing spontaneous movements of the eye which distracted the attention; also practice in the using of the ex-central portions of the retina, thus avoiding the insensitive fovea-centralis, appeared to increase the percentage of the flashes observed. In the case of the very faintest flashes the imagination of the experienced observers would naturally be more under control.

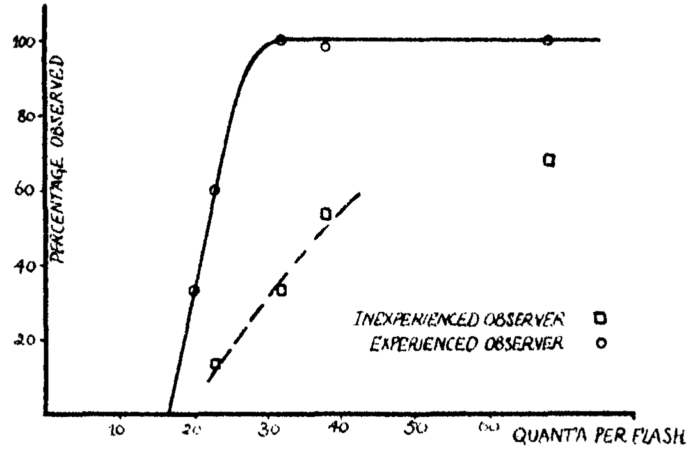

FIG. 5.

Fig. 6 shows the collected results of a dozen inexperienced observers. It will be seen that all the points except two lie beneath the curve for an experienced observer (shown in full), and these two can reasonably be ascribed to imagination.

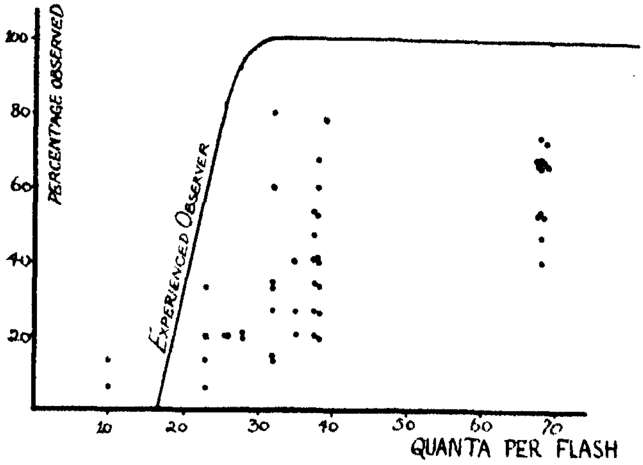

FIG. 6.

Table I shows the details of a set of trials by an experienced observer.

Table I.

| Slit width. | Duration of flash. | Area of telescope objective sq. cm. | Number of quanta per flash. | Number of consecutive flashes seen (maximum 3). | Percentage observed. |
|---|---|---|---|---|---|
| 2·7 cm. | 1·17 . $10^{-3}$ secs. | 4·53 | 73 | 3, 3, 3, 3, 3 | 100 |
| | | 2·51 | 40 | 3, 2, 3, 3, 3 | 93 |
| | | 2·01 | 32 | 3, 2, 3, 2, 3 | 87 |
| | | 1·54 | 25 | 2, 3, 2, 1, 2 | 67 |
| | | 1·32 | 22 | 1, 2, 1, 1, 0 | 33 |
| | | 0·91 | 15 | 0, 0, 0, 0, 0 | 0 |

For trained observers the limiting number of quanta observed in a flash of any duration less than 1/100 of second is 17. For untrained observers the limit might be estimated to lie between 30 to 35 quanta ($\lambda = 0\cdot505\ \mu$).

### *Effect of Duration of Flash.*

A series of experiments was carried out on the effect of the duration of the flash on the strength of the sensation produced. The "limit" was determined (with trained observers only) for duration of flash varying between 1 second and $4 \cdot 33 . 10^{-5}$ seconds. The results obtained are shown in fig. 7

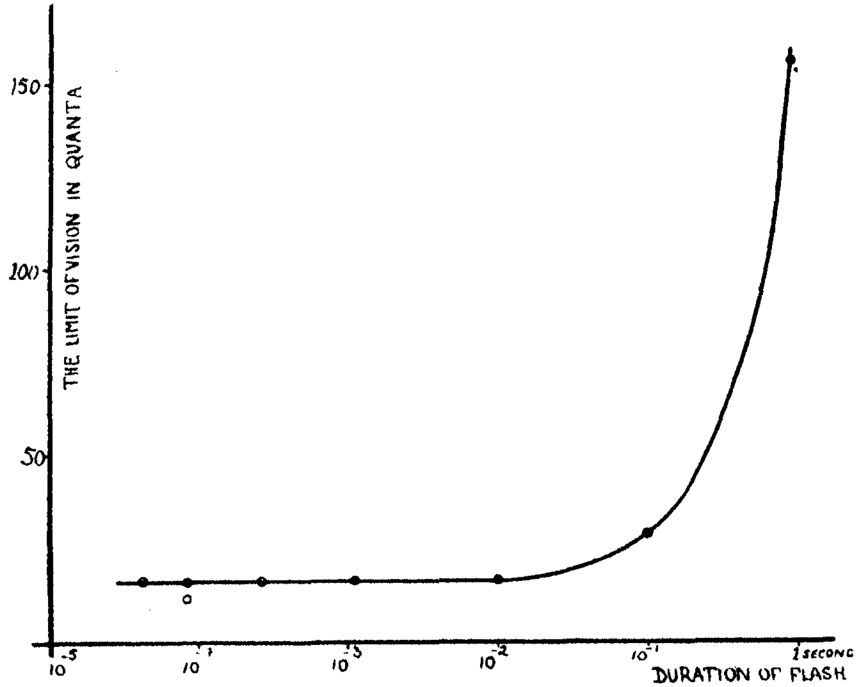

Fig. 7.

where the limit is plotted against duration of flash, and it is seen at once that the sensation for very short flashes depends only on the total energy in the flash and not on the duration. For long flashes the value of the limit approximates to the value obtained by Reeves* of 200 quanta per second for steady point sources (artificial stars). The two points corresponding to the shortest flashes could not be made with green light as the source of light was too weak. The filter was therefore removed, the trials carried out for white light, and the results evaluated for green light with the help of the scotopic luminosity curve.

### *Effect of Tonic Drug.*

It is known that under normal conditions the sensitivity of the human organism to external influences is not the greatest possible. The nerve impulses meet on their way to the brain certain resistances. There are, however, conditions when these resistances are partially removed and all the senses attain special sharpness. For example, 24 hours' starvation produces an increase in sensitivity. The same effect can be obtained more conveniently, however, by the injection or consumption of some "tonic" drug. It was interesting to see if a trained observer could improve his flash-sensitivity in such a way, or if the training itself consisted in diminishing the resistances mentioned. For this purpose a dose of strychnine (1/15 of a grain) was taken by an observer 1 hour before the experiment began. The results obtained showed that the limit was considerably lowered—to about 12 quanta. It must be mentioned, however, that only one such experiment was carried out and the result obtained is therefore not very reliable.

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* *Loc. cit.*

### *Summary of Part I.*

(1) An apparatus is described which produced regular point flashes of light of known spectral constitution, the energy in the flash and the duration being easily controlled.

(2) The minimum radiation visually perceptible was measured. The results giving 17 quanta of green light ($\lambda = 0 \cdot 5\ \mu$) for trained observers and 30 for untrained.

(3) The effect of the duration of a flash on its perceptibility was investigated with the result that for flashes of duration less than 1/100 of a second the energy in the flash only is important and not the duration. For longer flashes the limit approaches the value of 200 quanta per second given by Reeves.

(4) The influence of a tonic drug on the flash-sensitivity was investigated in a single case and it was found that the sensitivity was considerably increased.

# *Some Experiments Concerning the Counting of Scintillations Produced by Alpha Particles.—Part II. The Determination of the Efficiency of Transformation of the Kinetic Energy of α-Particles into Radiant Energy.*

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The efficiency of zinc-sulphide in transforming the energy of α-particles into radiant energy was first investigated by Marsden* who measured the amount of energy radiated as visible light from zinc-sulphide crystals bombarded by α-particles. The value of the efficiency obtained was 1·5 per cent. though he considered this an under-estimate.

The authors of this work were informed by Prof. Wertenstein, of Warsaw, that he had made some approximate determinations of the luminous efficiency of zinc-sulphide and obtained a very high value of 10 or 15 per cent. Prof. Wertenstein, however, considered these figures as merely a rough estimate and not necessarily reliable.

It will probably be useful to give here a definition of the expression "luminous efficiency." It can be written as a fraction, the numerator of which is "the brightness of the source of light," and the denominator the maximum brightness which can be obtained from the energy which is spent on the source.

The denominator is obviously equal to the power spent on the source, divided by the mechanical equivalent of light. The numerator can be measured visually or calculated, if the distribution and absolute values of the energy in the spectrum are known.

A calculation of the luminous efficiency of radioactive luminous paints, which are actually a mixture of a radioactive substance with zinc-sulphide, is given in Berndt's book "Radioaktive Leuchtfarben." The value obtained is 15 per cent.

## *Experimental Method.*

A determination of the luminous efficiency of the process of scintillation formation necessitates the measurement of the candle power of a zinc-sulphide screen when bombarded by a known number of α-particles of known energy.

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* 'Roy. Soc. Proc.,' vol. 83, p. 554 (1910).

The evaluation of the luminous energy from a source of known candle-power can readily be calculated in terms of mechanical units by the help of the mechanical equivalent of light.

There are two ways of measuring the candle-power of a zinc-sulphide screen. The simpler way is a visual comparison between the screen and some standard of candle-power, while the other is a determination of the spectral distribution of the energy radiated in absolute units, from which the candle-power may be calculated with the help of the equation which defines the mechanical equivalent of light, namely,

$$\int_0^\infty \mathrm{E}_\lambda \times \text{luminosity } \lambda \, d\lambda = \text{candle power} \times \text{mechanical equivalent of light.} \quad (1)$$

The latter method was chosen as being the most objective and therefore the most reliable. The former method was also used as a check on the values obtained by the latter method. A third method also was used to check the relative values of the efficiencies obtained for the various zinc-sulphides, which consisted of a measurement of the sensitivities of a photographic plate for different wave-lengths and of the total blackening produced in a photographic plate when illuminated directly by the light from a zinc-sulphide screen bombarded by $\alpha$-particles. Then, if the form of the energy distribution is known for any zinc-sulphide, the absolute values can be obtained by the help of the equation

$$\int_0^\infty \mathrm{E}_\lambda \times \text{sensitivity } \lambda = \text{integral blackening.}$$

The method which depends on a calculation of the candle-power of a zinc-sulphide screen from the results obtained for the spectral distribution of the radiant energy in absolute units will first be described.

In order to obtain the spectral distribution, spectrograms were taken of the various zinc-sulphides when bombarded by $\alpha$-particles. This necessitated a strong source of $\alpha$-rays with a conveniently long period.

An $\alpha$-ray tube filled with radon was consequently chosen. The tube could be covered with zinc-sulphide crystals and a spectrogram taken. The crystals could then be removed and the tube covered with a new preparation. In this way spectrograms of several different zinc-sulphides could be obtained on a single photographic plate.

Though the absolute values of the intensity of the radiation from the $\alpha$-ray tube for different wave-lengths can be calculated from the spectrograms obtained, as will be described in the sequel, the number and energy of the $\alpha$-particles producing the radiation could not be determined, owing to the irregularities of the glass walls of the tube. The brightness of the $\alpha$-ray tube was therefore compared with that of a plane screen of the same zinc-sulphide bombarded by a known number of $\alpha$-particles of known energy. The comparison of the brightnesses, since the spectral distributions were the same, could be made by simply comparing the blackenings produced in a photographic plate illuminated directly by the light from both sources.

In order to determine the spectral distribution of the energy radiated from the $\alpha$-ray tube in absolute units it was necessary to take spectrograms of some standard source of light of known spectral distribution and intensity, on the same photographic plate. The standard source of light used was a magnesium oxide screen illuminated by a 70 c.p. filament lamp of colour temperature 2660° abs. and standardised at the National Physical Laboratory. Several spectrograms of this standard source were taken on the same photographic plate with stops of various measured areas placed over the collimator lens, the duration of exposure in every case being the same as that for the $\alpha$-ray tube, namely, 40 minutes.

The function of the stops was to vary the area of the magnesium screen from which light could reach the photographic plate. For a given stop on the collimator lens, the amount of light falling on the photographic plate will be independent of the distance of the magnesium screen from the collimator slit, for the area of magnesium screen from which light can reach the photographic plate varies as the square of the distance from slit to screen, while the solid angle subtended by the slit at the screen varies inversely as the square of the distance. The spectrograms obtained in this way were microphotometered, and, in fig. 1, the results are shown, the blackening on the photographic plate being plotted against wave-length for each spectrogram. The wave-lengths were obtained from the lines of the sun spectra taken on the same plate, in the usual way. From these curves it can be seen that at the wave-lengths where a curve for a zinc-sulphide intersects one of the magnesium oxide curves, the blackenings, and therefore the energies falling on the photographic plate, are equal. Now though the energy falling on the photographic plate at a given wave-length from the magnesium oxide screen is not calculable, yet the candle-power of that area of the magnesium screen, effective in producing the blackening of the photographic plate, can be calculated from the area of stop on the collimator lens and the distance of the standard lamp from the magnesium screen. Also the intensity of the total radiation in that wave-

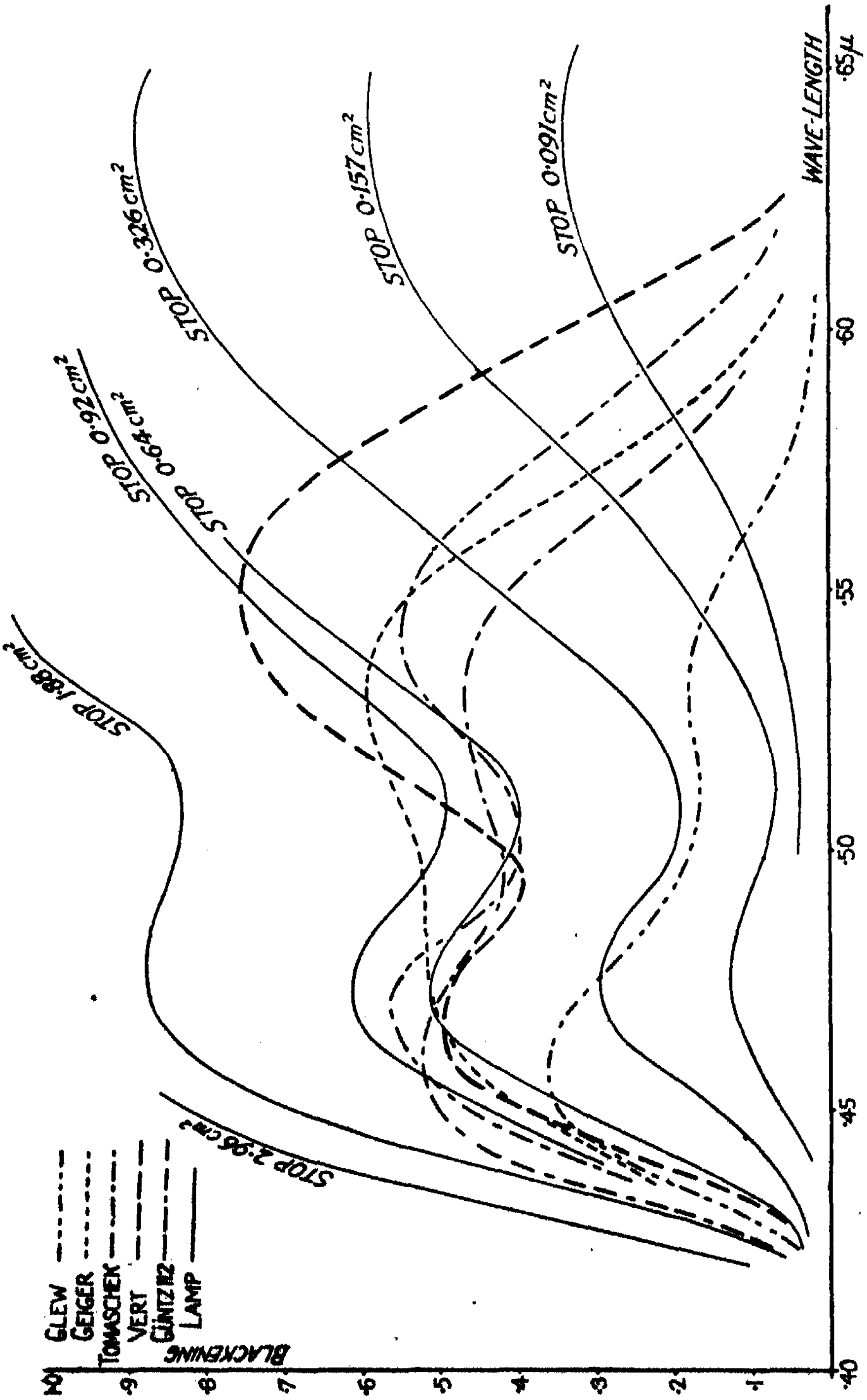
GLEW
GEIGER
TOMASCHEK
VERT
GÜNTZ №2
LAMP
BLACKENING
1·0
·9
·8
·7
·6
·5
·4
·3
·2
·1
·40
·45
·50
·55
·60
·65μ
WAVE-LENGTH
STOP 2·96 cm²
STOP 1·88 cm²
STOP 0·92 cm²
STOP 0·64 cm²
STOP 0·326 cm²
STOP 0·157 cm²
STOP 0·091 cm²

Fig. 1.

length from a source of known candle-power and colour temperature can be calculated, from Wien's formula

$$E_\lambda \, d\lambda = C_1 e^{-C_2/\lambda T} \, d\lambda, \tag{2}$$

and from equation (1).

Also the fraction of the total radiation from a source which falls on the photographic plate is inversely proportional to the square of its distance from the collimator slit. Hence a calculation of the absolute value of the intensity of the radiation from the radon tube, independent of all properties of the photographic plate, can be at once made for those particular values of $\lambda$ where an intersection occurs with one of the magnesium oxide curves of fig. 1. A similar calculation will give the intensity at intermediate wave-lengths when an interpolation has been made to determine that area of stop on the collimator lens which would have produced an intersection at that wave-length. Let us call this area of stop on the collimator lens "the equivalent area of stop" for wave-length $\lambda$.

The values of the intensities of the radiant energy in different wave-lengths can now be plotted against the wave-length, and a graphical integration of the area under the curve will give a value of the total energy radiated. Also the candle-power of the $\alpha$-ray tube can be calculated by graphical integration of the left-hand side of the equation (1).

### *Calculation of the spectral distribution of the energy radiated from the α-ray tube and of the candle-power for coverings of various zinc-sulphides.*

As we have seen, it is necessary to calculate the candle-power of that area of the magnesium oxide screen effective in producing the blackening of the photographic plate for each stop used on the collimator lens.

The normal candle-power per square centimetre of a magnesium oxide screen illuminated by a lamp of candle-power C placed at a distance D in a direction making an angle $\theta$ with the normal to the screen is $C \cos \theta / \pi D^2$.

If the focal length of the collimator lens of the spectrograph is $f$, and the area of the stop on the lens is S, then the area of the magnesium screen effective in producing the blackening of the photographic plate, when the screen is at a distance $d$ from the collimator slit, is $s \times d^2/f$, and the effective candle-power is therefore $C \cos \theta \, . \, sd^2/D^2 f = E$, say.

If, then, S is the "equivalent area of stop" at a certain wave-length $\lambda$ for a certain zinc-sulphide, then the intensity of the radiation of wave-length $\lambda$

from the α-ray tube will be the same as the intensity of the radiation of wave-length $\lambda$ in a source of colour temperature 2660° K. and candle-power

$$\mathrm{E} \,.\, d_1{}^2/d^2 = \text{say, A c.p.},$$

where $d_1$ is the distance at which the α-ray tube was placed when the spectrogram under consideration was taken. Now the experimental values were, $\mathrm{C} = 70$ c.p., $\theta = 35°$, $\mathrm{D} = 31 \cdot 8$ cm., $f = 28$ cm., and therefore $\mathrm{A} = 2 \cdot 32 \,.\, 10^{-5}\, sd_1{}^2$ c.p. Now we have seen in the first part of this paper that an evaluation of the left-hand side of the equation (1) for a source of colour temperature 2660° K. gives $\mathrm{C}_1 \times 1 \cdot 24 \,.\, 10^{-4}$ watts per unit solid angle, where $\mathrm{C}_1$ is the constant of Wien's formula. Consequently the value of $\mathrm{C}_1$ for a source of 2660° K. colour temperature can be at once calculated when the candle-power is known, for

$$\mathrm{C}_1 \times 1 \cdot 24 \,.\, 10^{-4} = \text{c.p.} \times \text{mechanical equivalent of light.}$$

Hence for a source of candle-power A, $\mathrm{C}_1 = 12 \cdot 9\, \mathrm{A}$, the units being such as to give $\int \mathrm{E}_\lambda \, d\lambda$ in watts per unit solid angle.

We have, then, that the value of $\mathrm{E}_\lambda d\lambda$ for the radiation from an α-ray tube when S is the "equivalent area of stop" and $d_1$ is the distance the α-ray tube was placed from the collimator slit, is given by

$$\mathrm{E}_\lambda \, d\lambda = 3 \cdot 0 \,.\, 10^{-4}\, sd_1{}^2 \,.\, e^{-5 \cdot 4/\lambda}\, d\lambda, \tag{3}$$

where the units of wave-length are microns.

Five different preparations of zinc-sulphides were used as coverings for the α-ray tube. The values obtained for "equivalent area of stop" at various wave-lengths are tabulated for each different covering. The values of $d_1$, the distance of the α-ray tube from the slit of the spectrograph, are given beneath the name of the zinc-sulphide preparation. Column two gives the values of the term $3 \cdot 0 \,.\, 10^{-4} e^{-5 \cdot 4/\lambda}$ for each wave-length and columns 8 to 12 give the values of $\mathrm{E}_\lambda$ calculated from the expression (3). · From these values of $\mathrm{E}_\lambda$ and the values of the luminosity for the scotopic eye, the value of the integral

$$\int_0^\infty \mathrm{E}_\lambda \text{ luminosity } \lambda \, d\lambda \text{ can be calculated in watts per unit solid angle,}$$

and the candle-power of the α-ray tube can be found from equation (1).

The results are shown in Table III, where the second column gives the value of $\int_0^\infty \mathrm{E}_\lambda$ luminosity $\lambda \, d\lambda$ which is the value of the luminous energy radiated

Table II.

| $\lambda$ $\mu\mu$ | $3 . 10^{-4} . e^{-6\cdot4/\lambda}$. | Equivalent area of stop. | | | | | $E_\lambda . 10^6$. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Glew $d_1 = 8\cdot3$ cm. | Geiger $d_1 = 8\cdot65$ cm. | Tomaschek $d_1 = 8\cdot2$ cm. | Vert $d_1 = 8\cdot6$ cm. | Güntz 112 $d_1 = 8\cdot25$ cm. | Glew. | Geiger. | Tomaschek. | Vert. | Güntz 112. |
| 422 | $5\cdot25 . 10^{-8}$ | 0·665 | 0·964 | 1·0 | 0·672 | 1·64 | 2·41 | 8·20 | 3·54 | 2·61 | 8·33 |
| 428 | $6\cdot3 . 10^{-8}$ | 0·839 | 0·80 | 0·87 | 0·533 | 1·63 | 3·57 | 3·77 | 3·69 | 2·48 | 7·0 |
| 434 | $7\cdot2 . 10^{-8}$ | 0·99 | 1·04 | 1·16 | 0·741 | 1·57 | 4·8 | 5·60 | 5·6 | 3·95 | 7·7 |
| 440 | $8\cdot7 . 10^{-8}$ | 0·828 | 0·88 | 0·932 | 0·742 | 1·41 | 4·95 | 5·72 | 5·44 | 4·79 | 8·35 |
| 447 | $9\cdot45 . 10^{-8}$ | 0·776 | 0·862 | 1·05 | 0·828 | 1·24 | 5·02 | 6·10 | 6·65 | 5·78 | 7·95 |
| 454 | $10\cdot5 . 10^{-8}$ | 0·632 | 0·80 | 0·98 | 0·851 | 1·07 | 4·55 | 6·27 | 6·91 | 6·61 | 7·6 |
| 463 | $12\cdot3 . 10^{-8}$ | 0·271 | 0·665 | 0·830 | 0·720 | 0·775 | 2·30 | 6·12 | 6·87 | 6·55 | 6·48 |
| 472 | $14\cdot1 . 10^{-8}$ | 0·346 | 0·624 | 0·763 | 0·600 | 0·600 | 3·36 | 6·59 | 7·25 | 6·25 | 5·74 |
| 481 | $15\cdot6 . 10^{-8}$ | 0·28 | 0·686 | 0·65 | 0·561 | 0·567 | 3·00 | 8·0 | 6·78 | 6·51 | 6·0 |
| 491 | $17\cdot7 . 10^{-8}$ | 0·270 | 0·802 | 0·602 | 0·550 | 0·585 | 3·29 | 10·6 | 7·12 | 7·22 | 7·02 |
| 502 | $20\cdot4 . 10^{-8}$ | 0·275 | 0·95 | 0·62 | 0·72 | 0·70 | 3·85 | 14·5 | 8·48 | 10·9 | 9·7 |
| 514 | $23\cdot4 . 10^{-8}$ | 0·27 | 1·0 | 0·667 | 0·95 | 0·692 | 4·34 | 17·5 | 10·5 | 16·5 | 11·0 |
| 527 | $26\cdot7 . 10^{-8}$ | 0·25 | 0·82 | 0·63 | 1 | 0·59 | 4·61 | 16·4 | 11·3 | 19·8 | 10·75 |
| 542 | $30\cdot9 . 10^{-8}$ | 0·165 | 0·552 | 0·528 | 0·852 | 0·411 | 3·51 | 12·7 | 10·0 | 19·5 | 8·65 |
| 558 | $35\cdot7 . 10^{-8}$ | 0·095 | 0·311 | 0·345 | 0·637 | 0·235 | 2·34 | 8·3 | 8·28 | 16·8 | 5·7 |
| 575 | $40\cdot8 . 10^{-8}$ | 0·05 | 0·13 | 0·17 | 0·325 | 0·1 | 1·40 | 3·97 | 4·63 | 9·85 | 2·76 |
| 596 | $46\cdot8 . 10^{-8}$ | — | 0·076 | 0·07 | 0·121 | 0·060 | — | 2·65 | 2·2 | 4·2 | 1·91 |
| 618 | $53\cdot7 . 10^{-8}$ | — | — | 0·04 | 0·06 | 0·03 | — | — | 1·44 | 2·38 | 1·09 |

from the $\alpha$-ray tube evaluated as green light of wave-length, $0 \cdot 505\ \mu$, for the various coverings of the $\alpha$-tube which give at once the candle-power on dividing by the mechanical equivalent of light in watts per lumen.

Table III.

| Zinc-sulphide. | $\int_0^\infty E_\lambda \times$ luminosity $\lambda$ $d\lambda$ watts/unit solid angle ($\lambda = 0 \cdot 505\ \mu$). | Candle-power of $\alpha$-ray tube. | $\int_0^\infty E_\lambda\, d\lambda$. |
|---|---|---|---|
| Glew | $3 \cdot 20 \,.\, 10^{-7}$ | $2 \cdot 0 \,.\, 10^{-4}$ | $0 \cdot 58 \,.\, 10^{-6}$ |
| Geiger | $9 \cdot 81 \,.\, 10^{-7}$ | $6 \cdot 13 \,.\, 10^{-4}$ | $1 \cdot 65 \,.\, 10^{-6}$ |
| Tomaschek | $7 \cdot 41 \,.\, 10^{-7}$ | $4 \cdot 64 \,.\, 10^{-4}$ | $1 \cdot 38 \,.\, 10^{-6}$ |
| Vert | $1 \cdot 015 \,.\, 10^{-6}$ | $6 \cdot 34 \,.\, 10^{-4}$ | $1 \cdot 90 \,.\, 10^{-6}$ |
| Güntz 112 | $7 \cdot 17 \,.\, 10^{-7}$ | $4 \cdot 48 \,.\, 10^{-4}$ | $1 \cdot 33 \,.\, 10^{-6}$ |

The fourth column gives the values of the integrals

$$\int_0^\infty E_\lambda\, d\lambda,$$

which is the value of the total energy radiated from the $\alpha$-ray tube in watts per unit solid angle.

As it has already been pointed out the numbers and energies of the $\alpha$-particles bombarding the zinc-sulphide on the surface of the $\alpha$-ray tube could not be determined with any precision. It was necessary, therefore, to make a comparison between the brightness of the $\alpha$-ray tube and that of a plane screen of the same zinc-sulphide on which $\alpha$-particles were falling with known energy and in measurable numbers. Since the spectral distributions of the light are the same in both cases, the intensities could be compared by comparing the blackening in a photographic plate illuminated directly by light from the two sources.

Since the light from zinc-sulphide crystals under heavy bombardment gradually decreases with time owing to the destruction of the crystals,* it was necessary to make the comparison at the same time as the spectrograms.

Half of a photographic plate (Ilford Monarch) was covered with an optical step wedge and exposed to the direct light from the $\alpha$-ray tube while each spectrogram was being taken, the other half of the photographic plate being laid aside for exposure to the light from the plane screen of the same zinc-sulphide as covered the $\alpha$-ray tube.

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* Marsden, *loc. cit.*

The optical step wedge was similar to the one used in the experiments described in Part I. The plane screens used were made of thick layers of zinc-sulphide crystals to ensure that there were no spaces through which an $\alpha$-particle could pass without forming a scintillation and to ensure that all the energy of the $\alpha$-particle was lost in the zinc-sulphide. The screens were covered by a black paper diaphragm to limit the area bombarded by $\alpha$-particles. A polonium source of $\alpha$-particles was used which was held rigidly in a brass holder to which the black paper diaphragm was pasted. This enabled the source to be moved from one zinc-sulphide screen to another without altering the relative positions of the source of $\alpha$-particles, and the portion of the screen bombarded. The photographic plate was then placed above the screen. The exposure was of the same duration as the exposure of the other half of the photographic plate to the $\alpha$-ray tube. The two halves of the plate were then developed and fixed together and microphotometered. The blackening on the plate exposed to the $\alpha$-ray tube was plotted against the transmissivity of the various steps of the optical wedge. The transmissivity which would have reduced the blackening to the same value as that produced by the plane screen on the other half of the plate could then be at once determined by intrapolation. The relative brightnesses of the $\alpha$-ray tube and screen could thus be calculated from their distances from the photographic plate.

In practice, in order to ensure that the blackening of the plate exposed to the plane screen was intermediary to those on the plate exposed through the optical step wedges, both halves of the plate were again cut in half, the one exposed to the $\alpha$-ray tube, after exposure, and the other before exposure. This enabled a second comparison to be made if the first one was unsatisfactory. If $t$ is the transmissivity of the optical wedge which would have made the blackenings in each case equal, and if $d_a$ is the distance of the $\alpha$-ray tube from the photographic plate and $d_p$ the distance of the plane screen to the plate, then the candle-power of the plane screen is given by

$$C_p = C_a \, t \, (d_p/d_a)^2,$$

where $C_a$ is the candle-power of the $\alpha$-ray tube.

Table IV gives the experimental values of these quantities for the various zinc sulphides, the values of the candle-powers of the plane screens being given in the last column but one.

The factor $t_a \, (d_p/d_a)^2$ also connects the total energy radiated in unit solid angle from the plane screen with that radiated from the $\alpha$-ray tube. Hence, multiplying the values in column four of Table III by this factor, we obtain the value of the total energy radiated from the plane screen in watts per unit solid angle. The values obtained are tabulated in column seven of Table IV.

Table IV.

| Zinc-sulphide. | $C_a$. | $t$. | $d_p$ cms. | $d_a$ cms. | $C_p$. | $\int E_\lambda \, d\lambda$ for plane screen in watts/units solid angle. |
|---|---|---|---|---|---|---|
| Glew ............... | $2\cdot0 \;. 10^{-4}$ | 0·11 | 4·2 | 70·5 | $7\cdot8 \;. 10^{-8}$ | $2\cdot3 \;. 10^{-10}$ |
| Geiger ............ | $6\cdot13 \;. 10^{-4}$ | 0·082 | 4·2 | 70·6 | $1\cdot78 \;. 10^{-7}$ | $4\cdot8 \;. 10^{-10}$ |
| Tomaschek .... | $4\cdot64 \;. 10^{-4}$ | 0·042 | 4·2 | 70·3 | $6\cdot94 \;. 10^{-8}$ | $2\cdot1 \;. 10^{-10}$ |
| Vert ............... | $6\cdot34 \;. 10^{-4}$ | 0·082 | 4·2 | 70·6 | $1\cdot84 \;. 10^{-7}$ | $5\cdot5 \;. 10^{-10}$ |
| Güntz 112........ | $4\cdot48 \;. 10^{-4}$ | 0·121 | 4·2 | 70·2 | $1\cdot94 \;. 10^{-7}$ | $5\cdot75 \;. 10^{-10}$ |

In order to determine the number of α-particles falling on the plane screens, it was necessary to measure the number of α-particles emitted by the source, and also to measure the solid angle subtended by the screen at the source.

The number of α-particles emitted by the source was measured by counting the scintillations on a screen placed at a known distance from the source *in vacuo*. In this case, however, the screen consisted of a thin layer of crystals and it was therefore necessary to measure the effective area of the screen. This was accomplished by counting the number of scintillations produced on the same screen by a source of radium active deposit whose γ-ray activity had previously been measured. A simple correction was made for any active deposit which was attached to parts of the source from which the α-particles could not reach the screen by counting with the source reversed. Both the polonium and the radium active deposit sources were so large that it was necessary to reduce the number of scintillations observed on the screen by rotating a brass wheel with a sector of 7·2° cut out of it, between the screen and the microscope objective. The speed of rotation was more than 10 revolutions per second, so that the screen did not appear to flicker. The actual fraction by which the number of scintillations were reduced was not important as the conditions of counting were the same for each source.

The total number of α-particles emitted from the polonium source was found to be $1\cdot09 \;. 10^7$ per second. The solid angle subtended by the screen at the source was calculated from measurements made with a travelling microscope and found to be 0·027. Thus the number of α-particles falling on the screen per second was $2\cdot34 \;. 10^4$.

The distance from the centre of the screen to the source was 1·50 cm., thus the range of the polonium particles striking the screen was 2·4 cm., and applying Geiger's cube law to determine the velocity, the energy of the particles is seen to be 6·32 . $10^{-6}$ erg. Thus the total energy falling on the screen was 0·148 erg per second.

Now $C_p$ is the normal candle-power of the plane screens, and hence if the screen radiates uniformly in all directions, the total energy radiated evaluated as green light, will be $4\pi C_p$ × mechanical equivalent of light in energies per second per lumen. As was previously mentioned, however, the plane screens used were made of thick layers of crystals in order that the α-particles should lose all their energy in the zinc-sulphide. Consequently, the light of the scintillations produced in the upper layers of the zinc-sulphide is not distributed uniformly over a sphere, but part of the light directed into the screen is thrown back, thus increasing the brightness of the screen observed from above.

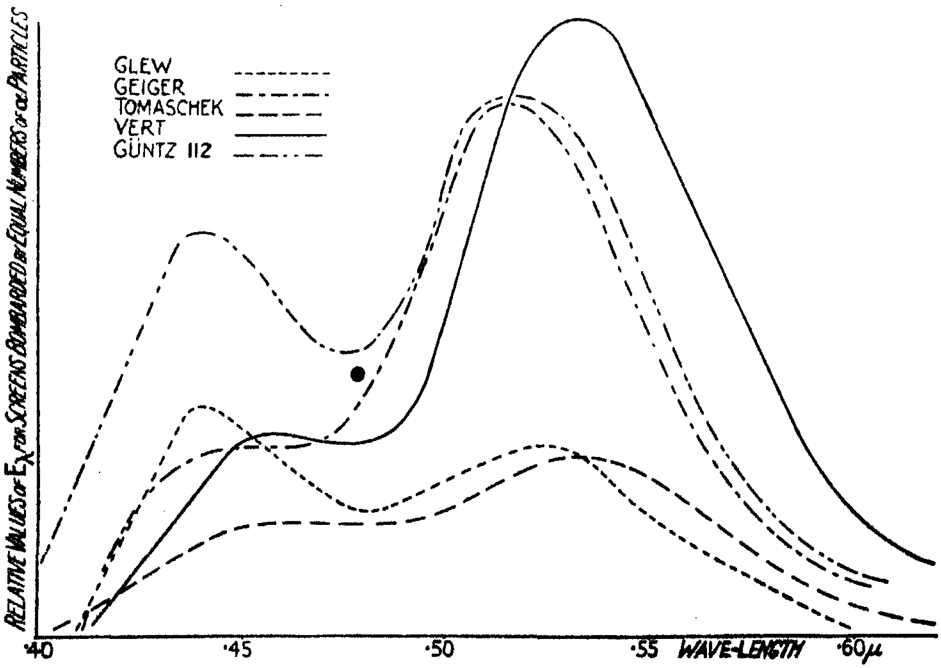

FIG. 2.

If it be assumed that the light is diffused more or less according to Lambert's law and allowance be made for absorption in the crystals, the amount of light scattered upwards by the lower layers in a direction normal to the screen will be practically equal to the amount originally directed downwards from the surface layers. Consequently, the total light radiated from the screen, evaluated as green light, will be $2\pi C_p \times$ mechanical equivalent of light in energies per second per lumen, and the values of the luminous efficiencies will be given by

$$\frac{2\pi C_p}{0\cdot148} \times \text{mechanical equivalent of light},$$

where 0·148 erg is the value obtained for the total kinetic energy of the $\alpha$-particles falling on the screen per second.

In Table V are shown the values of $C_p$ taken from Table IV, and also the values of the luminous efficiencies for the various zinc-sulphides.

The values of the radiant efficiencies can at once be obtained from column 7, Table IV, which gives the values of the total energy W, radiated normally from the screen in watts per unit solid angle. In this case the radiant efficiency R is $2\pi W \times 10^{-7}/0\cdot148$. The values of W and the radiant efficiency from the various zinc-sulphides are tabulated in the third and fourth columns of Table V.

Table V.

| Zinc-sulphides. | $C_p$. | W. | Radiant efficiency. | Luminous efficiency. |
|---|---|---|---|---|
| | | | Per cent. | Per cent. |
| Glew | $0\cdot78 \,.\, 10^{-7}$ | $2\cdot3 \,.\, 10^{-10}$ | 9·8 | 5·3 |
| Geiger | $1\cdot78 \,.\, 10^{-7}$ | $4\cdot8 \,.\, 10^{-10}$ | 20·5 | 12·1 |
| Tomaschek No. 10* | $0\cdot70 \,.\, 10^{-7}$ | $2\cdot1 \,.\, 10^{-10}$ | 9·0 | 4·8 |
| Vert | $1\cdot84 \,.\, 10^{-7}$ | $5\cdot5 \,.\, 10^{-10}$ | 23·5 | 12·5 |
| Güntz 112 | $1\cdot94 \,.\, 10^{-7}$ | $5\cdot8 \,.\, 10^{-10}$ | 25·0 | 13·2 |

* The value of Tomaschek No. 10 is probably low owing to the fact that a thin screen was used as the supply of this sample was scarce.

### *Visual Determination of the Luminous Efficiency of One Zinc-sulphide.*

It seemed desirable to obtain a check on the value of the luminous efficiency by some simple method. All that is necessary for a determination of the luminous efficiency is a measurement of the candle-power of a zinc-sulphide screen bombarded by a known number of $\alpha$-particles of known energy. In this method the same screen of Güntz 112 zinc-sulphide and the same polonium source were used as in the last experiment, and the relative positions were kept the same. Thus the value of the energy falling on the screen could be taken from the measurements of the last experiment, namely, 0·148 erg per second. The candle-power of this screen was measured by comparing it with a magnesium oxide screen A, illuminated by the light diffused from another magnesium oxide screen B illuminated by light from a 70-c.p. lamp. The distance between the screens A and B could be adjusted until the screen A and the magnesium screen appeared of equal surface brightness. The candle-power of the screen A could at once be calculated from the geometry of the arrangement.

The standard lamp (70-c.p.) was placed at a distance of 91·4 cm. from the screen B and in a direction making an angle of 45° with the normal to B, whose surface area was 2 sq. cm. The screen A, when adjustment had been made for equal surface brightness of A and the zinc-sulphide screen, was found to be at a distance of 15·5 cm. from B, and in a direction such that the line joining A and B made an angle of 10° with the normal to each. The normal candle-power of B was therefore $3 \cdot 77 \,.\, 10^{-3}$ c.p. The normal candle-power of A was therefore $4 \cdot 85 \,.\, 10^{-6}$ c.p.

But the area of the zinc-sulphide screen was 0·1 sq. cm. and its candle-power was, therefore, $4 \cdot 85 \,.\, 10^{-7}$ c.p., which gives for the luminous efficiency the value 33 per cent.

No great weight can be attached to the result of so rough a method which depends on a visual comparison of faint sources of light of widely different colours. The interest of the result, however, lies in the fact that it is still higher than the strikingly high values obtained by the previous method.

### *Determination of the Relative Luminous Efficiencies by Photographic-blackening Method.*

This method depended upon the previous measurement of the spectral distribution of the energy radiated from the various zinc-sulphides, together with a determination of the relative sensitivities of a photographic plate for lights of different wave-lengths. When both of these were known, it was possible to calculate the relative blackenings which would be produced in a photographic plate illuminated directly by light from screens of different zinc-sulphide, but of the same candle-power. Thus a determination of the relative blackenings produced by screens of different zinc-sulphide bombarded by equal numbers of α-particles enabled relative values of the luminous efficiency to be calculated.

The relative sensitivities of a photographic plate for different wave-lengths were determined by taking faint spectrograms of a source of known spectral distribution, in this case a magnesium oxide screen illuminated by a 70-c.p. lamp of colour temperature 2660° K. On microphotometering the spectra and dividing the blackening at each wave-length by the intensity of the radiant energy of that wave-length in a source of 2660° K. and multiplying by the relative dispersion of the spectrograph used for that wave-length, the relative sensitivities were calculated. These values of the sensitivities will only be correct when there is no selective absorption in the prism or lenses of the spectrograph. The actual prism used was one of heavy lead glass and had a stronger absorption in the blue than in the red part of the spectrum. This fact will be discussed later in connection with the results obtained.

On multiplying the values of $E_\lambda$ given in columns 8 to 12 of Table II by the values of the relative sensitivities at corresponding wave-lengths, and plotting these products against the wave-length for each zinc-sulphide, graphical integration gives the relative blackenings which would be produced in a photographic plate illuminated directly by screens of the various zinc-sulphides with the candle-powers of the $\alpha$-ray tubes calculated in column 3 of Table III.

Dividing the values obtained by graphical integration by the candle-power given in column 3 of Table III we obtain the relative blackenings Q produced in a photographic plate illuminated by light from screens of various zinc-sulphides but of the same candle-power. Or expressed mathematically

$$Q = \int_0^\infty E_\lambda \times \text{relative sensitivity } d\lambda \bigg/ \int_0^\infty E_\lambda \times \text{luminosity } \lambda\, d\lambda.$$

Portions of a photographic plate were exposed directly to the light from the zinc-sulphide screens when bombarded by $\alpha$-particles from polonium in the same way as in the previous experiments, the number of $\alpha$-particles and the size of the screen being the same for each zinc-sulphide. This plate was developed and fixed together with the plate on which the spectrograms were taken for a determination of the relative sensitivities and then microphotometered.

Dividing the blackening B obtained in each portion of the plate by the value of Q for the corresponding zinc-sulphide values were obtained which were proportional to the luminous efficiencies of the zinc-sulphide.

Care was taken in these measurements to ensure that all blackenings measured were slight and therefore could be taken proportional to the expression $\int E_\lambda \times \text{sensitivity } \lambda\, d\lambda$.

The Table VI gives the values of Q and B for the various zinc sulphides and the value of the ratio B/Q. The values given for these quantities in the table have no absolute meaning, the values of B given being the actual photometer readings. In the fifth column are given the relative values of B/Q when the value for Güntz 112 zinc-sulphide is put equal to unity. In the sixth column are given the values of the relative luminous efficiency calculated from the values obtained by the first method when the value for Güntz 112 is put equal to unity.

Table VI.

| Zinc-sulphide. | Q. | B. | B/Q. | Relative B/Q 112 = 1. | Relative luminous efficiency Güntz 112 = 1. |
|---|---|---|---|---|---|
| Glew | 780 | 7·12 | 0·914 | 0·50 | 0·40 |
| Geiger | 582 | 9·12 | 0·157 | 0·875 | 0·92 |
| Tomaschek No. 10 | 710 | 5·35 | 0·754 | 0·42 | 0·36 |
| Vert | 655 | 9·05 | 1·38 | 0·766 | 0·95 |
| Güntz 112 | 704 | 12·65 | 1·80 | 1·0 | 1·0 |

The disagreement in the case of the Vert zinc-sulphide between the values obtained for the luminous efficiency relative to Güntz 112 = 1, can be explained by the fact that the prism of the spectrograph absorbed an appreciable amount of the blue light falling on it. The spectrograms will give too low values for the relative sensitivities of the photographic plate for wave-lengths in the blue region. Thus the zinc sulphides which have a large fraction of the total energy in the yellow region of the spectrum when compared with Güntz 112 zinc-sulphide will appear to have low values of the relative efficiency.

A considerably larger fraction of the radiant energy is situated in the yellow end of the spectrum in the case of Vert zinc-sulphide than in the case of Güntz 112 zinc-sulphide, as will be seen by reference to fig. 2, where the spectral distributions are plotted for the various zinc-sulphides.

## *Summary.*

A determination has been made of the radiant and luminous efficiencies of various zinc-sulphides when bombarded by α-particles. Surprisingly high values were obtained, namely, about 25 per cent. and 12 per cent. respectively, while the value obtained by Marsden for the radiant efficiency was 1·5 per cent. These high values are, however, in agreement with those calculated by Berndt from data concerning radioactive luminous paints. Two rough methods were used to check the results obtained.

# *Some Experiments Concerning the Counting of Scintillations Produced by Alpha Particles.—Part* III. *Practical Applications.*

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## A.—INVESTIGATION OF THE INFLUENCE OF THE OPTICAL SYSTEM USED ON THE VISIBILITY OF SCINTILLATIONS.

There are two important characteristics of the microscope or any other optical system used for scintillation counting, which may influence the number observed, namely, the numerical aperture and the magnification. In order to show clearly the rôle of each factor it seemed desirable to investigate how the percentage of the number of particles observed varied with the numerical aperture in two cases where the magnification was widely different. The first case chosen was the counting of scintillations with a microscope of magnification 50, where the numerical aperture could be varied at will by placing stops on the objective. Stops of black paper which fitted the objective and could be easily interchanged in the dark were used.

The numerical aperture corresponding to each objective stop was measured in the usual way (see, for example, 'Dictionary of Applied Physics,' vol. 4, p. 205 (1923)). The importance of the numerical aperture is not due to its influence on resolving power, but to its influence on the fraction of the light from a scintillation which enters the objective. From the definition of numerical aperture it follows that the fraction of the light entering the objective from the object viewed is $\frac{1}{2}(1 - \sqrt{1 - (n \, . \, a)^2})$.

The results obtained are shown in fig. 1 (full curve), where the percentage of the scintillations produced by α-particles of 2·7 cm. range, which were observed, is plotted as ordinate against the fraction of the total light from a scintillation, which is captured by the microscope objective, as abscissæ. The manner in which the number of scintillations produced by a beam of α-particles falls off as the fraction of the light entering the eye is reduced has also been investigated by B. Karlik,[*] who observed the scintillations produced by α-particles of 3·5 cm. range with a microscope of numerical aperture 0·7, and reduced the light entering the eye by photographic plates placed between the objective and the eyepiece. Her results are shown by the second curve in fig. 1. There is a considerable difference between the results obtained by B. Karlik and those obtained here. In both cases Güntz 112 zinc-sulphide was used, with crystals of average diameter about 25 μ. The magnification of the optical system was also very similar. It is difficult to suggest a reason for the divergence, the only difference between the methods being the device used for reducing the fraction of the light from a scintillation which entered the eye.

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[*] 'Wien. Akad. Ber.,' vol. 136, p. 531 (1927).

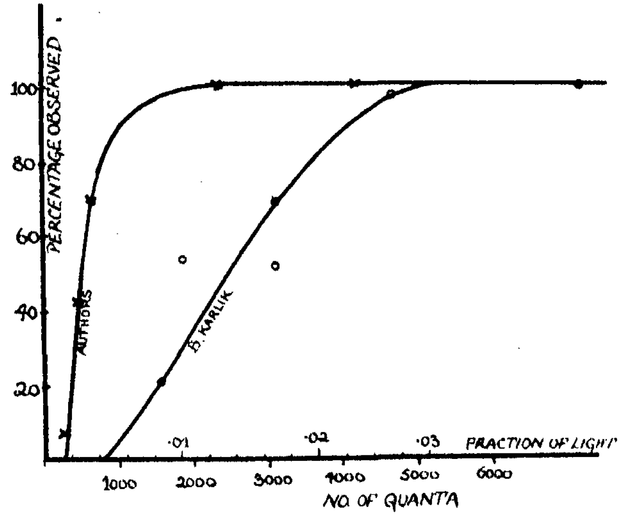

Fig. 1.

In order to assist the visualisation of these results a second scale of abscissæ is shown which gives in each case the number of quanta, evaluated as green light ($\lambda = 0\cdot505\ \mu$), entering the eye from a single scintillation. This scale was calculated by using the value of 13 per cent. for the luminous efficiency of Güntz 112 zinc-sulphide, obtained in Part II of this paper, and assuming that 20 per cent. of the light falling on the objective of a microscope does not reach the eye.

The variation with numerical aperture of the number of scintillations observed was also investigated in the case where the magnification was approximately unity. The scintillations were observed with the naked eye, and the percentage observed when the eye was placed at various distances from the screen was estimated. Altering the distance of the eye from the screen will, of course, change the magnification as well as the fraction of the light from a scintillation which enters the eye, but to a much smaller degree. The fraction of the light which enters the eye varies as the square of the distance, while the magnification varies as the first power.

An attempt was made to count the number of scintillations visible when the eye was placed at various distances from the screen, but this was found to be impossible as the eye became fatigued too quickly. Two possible reasons for this might be the difficulty of keeping the eye focussed at a definite distance and the small angle subtended at the eye by the screen. When observing scintillations with a microscope the focussing is so adjusted that the eye views the scintillations when it is completely relaxed. This fact enables the scintillations to be seen quite sharply over a long period without the eye becoming fatigued. Consequently a trial was made to see whether counting with a lens of 25 cm. focal length would be practicable. It was still, however, impossible to count, even when the scintillations appeared quite bright.

The percentage of scintillations observed at each distance was therefore estimated by a short glance at the screen, the total number being estimated by observing with a short focus lens with which the scintillations could be seen without difficulty.

The estimation of large numbers of scintillations by rapid glances is not so unreliable as it might seem. An accuracy of about 20 per cent. can usually be obtained when the number of scintillations is large. The accuracy of such counting in the field of view of a microscope was tried several times where a strong source of short period was used to produce scintillations. An estimate of the number at various times was made and a calculation of the true number made subsequently when the source had decayed sufficiently to make precise counting possible.

The use of a screen which would subtend a large angle at the eye was not attempted as the bombardment of it by $\alpha$-particles of definite range would have necessitated a special arrangement, while a simple estimation on a small screen gave results which could be considered as sufficiently accurate for the purpose.

The results are given in Table VII where the percentage observed, the fraction of light from the scintillation which enters the eye (area of pupil when eye is dark adapted $= 0\cdot57$ cm.,[*] and the corresponding radiant energy evaluated as green light ($\lambda = 0\cdot505\ \mu$) are tabulated for various distances of the eye from the screen.

Comparing this table with the curve in fig. 1, it is at once seen that a smaller fraction of the light from a scintillation produces a sensation when the eye is unaided than when a microscope is used. The limit visible in these two cases is seen to be 300 quanta and 30 quanta.

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[*] W. H. Steavenson, 'J. Br. Ast. Assoc.,' vol. 26, p. 303 (1916).

Table VII.

| Distance eye → screen. | Percentage observed. | Fraction of light entering the eye from a scintillation. | Corresponding number of quanta ($\lambda = 0 \cdot 505\ \mu$). |
|---|---|---|---|
| cm. | Per cent. | | |
| 10 | 100 | $4 \cdot 5 . 10^{-4}$ | 195 |
| 17 | 40 | $1 \cdot 57 . 10^{-4}$ | 68 |
| 25 | 5 | $0 \cdot 726 . 10^{-4}$ | 32 |

## B.—DETERMINATION OF THE VELOCITY OF THE SLOWEST α-PARTICLES CAPABLE OF PRODUCING A VISIBLE SCINTILLATION.

Some information concerning the visibility of scintillations produced by slow α-particles can be obtained from the works of Geiger* and Marsden and Taylor,† who used a magnetic field for the measurement of the velocities of the α-particles and detected them by the scintillation method.

Geiger, while investigating the change in velocity of an α-particle passing through mica, found that the scintillations produced by α-particles having a velocity equal to $0 \cdot 27\ V_0$ (where $V_0$ is the initial velocity of the radium C. α-particle) were on the limit of visibility.

Marsden and Taylor found, when carrying out somewhat similar experiment, that as they increased the thickness of mica covering the source, the particles were deflected more and more in the magnetic field until a point was reached where the velocity of the particles was $0 \cdot 415\ V_0$, after which on increasing the thickness of the mica the α-particles were not deflected further, but their numbers began steadily to decrease. The conditions under which the experiments were made would lead one to suspect, however, that the scintillations observed were produced by singly charged particles, the existence of which was unsuspected at that time. This would mean that the velocity of the particles observed was really $0 \cdot 21\ V_0$.

The scintillations produced by α-particles of considerably lower velocities were detected by Rutherford in his experiment on the capture and loss of electrons by α-particles.‡

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* 'Roy. Soc. Proc.,' A, vol. 83, p. 505 (1910).

† 'Roy. Soc. Proc.,' A, vol. 88, p. 443 (1913).

‡ 'Phil. Mag.,' vol. 47, p. 282 (1924).

Rutherford considered that $0 \cdot 25\ V_0$ is the smallest velocity at which scintillations can be conveniently counted, though they could still be observed when the velocity of the particles was as low as $0 \cdot 15\ V_0$. Counting was, however, difficult at this velocity.

A brass box B, fig. 2, one end of which was covered with a thick glass plate P with a zinc-sulphide screen attached to the inner surface, was placed between the poles of an electromagnet and evacuated by means of a mercury diffusion pump with a rotary oil pump to produce the fore-vacuum.

The source of $\alpha$-particles was a platinum wire of from 0·1 to 0·5 mm. in diameter which had been exposed to radon. The wire was held in position parallel to the magnetic field by a small holder H capable of being rotated about an axis passing through the wire. Rotation was effected by a screw S which pushed against a lever *l* attached to the holder. The screw could be operated *in vacuo* by turning a ground glass joint J.

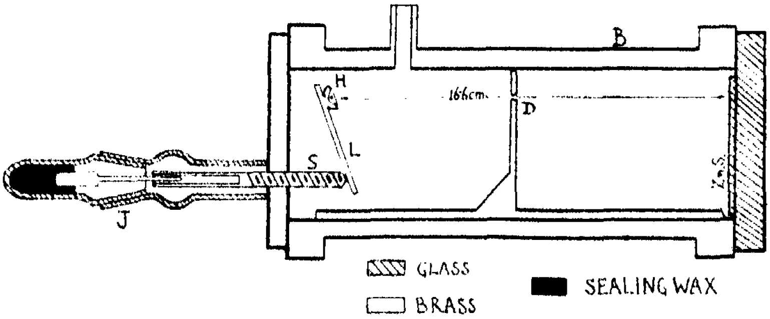

FIG. 2.

A small sheet of mica of stopping power 5·2 cm. was placed over the source and attached to the holder in such a way that the source was contained in a small air-tight chamber, which prevented contamination of the apparatus by radon. Rotation of the holder altered the distance traversed in the mica by $\alpha$-particles proceeding in any definite direction. A brass screen D was placed half-way between the source and the zinc-sulphide screen. A slit was made in it in such a way as to be parallel to the source and in the same horizontal plane. The slit was 0·3 mm. wide and 8 mm. long. Scintillations were observed through a microscope which could be moved in a vertical plane. A diaphragm was placed in the eyepiece of the microscope so that only a narrow horizontal strip of the screen was visible at each setting of the microscope. A pointer fixed to the microscope travelled on a vertical scale which enabled the position of the scintillations under observation to be measured relative to the source and slit whose positions had been previously measured.

From these relative positions the radius of curvature of the path of the $\alpha$-particle could be determined by geometry and when the value of the field was known the velocity could be calculated.

In order to reduce scattering of the $\alpha$-particles the walls of the box between the source and slit were lined with graphite and a liquid air trap was used to prevent mercury vapour entering the box.

If the $\alpha$-particles which passed through the mica in a given direction emerged with a perfectly definite velocity, then for each setting of the holder and each value of the magnetic field $\alpha$-particles would strike the screen in a band with definite velocity. By gradually altering the field it would be possible slowly to reduce the velocity of the particles striking the screen till the scintillations disappeared. Three complicating factors, however, make impossible so simple a procedure.

Firstly, the straggling of $\alpha$-particles in a sheet of mica of 5·2 cm. stopping power is considerable. Consequently, if for a given direction through the mica the particles with the mean velocity will pass through the slit, then among particles which pass through the mica in directions on each side of this given direction a certain number having velocities suitably different from the mean will also be able to pass through the slit. Thus straggling in the mica will prevent the formation of a narrow band of scintillations and allow $\alpha$-particles of a considerable range of velocities to strike the screen, the number having a given velocity being a maximum at some special value of the velocity and falling off on each side. But since all the $\alpha$-particles come from the source and pass through the slit, straggling will not influence the resolution of the $\alpha$-particles according to their velocities. Hence a wide band of scintillations will be formed on the screen, the number at a given point of the screen having a maximum at some definite part of the screen and falling off on each side in the form of a probability curve.

The second complication arises owing to the fact that the $\alpha$-particles which pass through the mica will have a probability of capturing an electron and so losing one charge. Also the probability of an $\alpha$-particle losing a charge will depend on the distance travelled in the mica, and, therefore, will be a function of their velocity on emerging from the mica. Consequently, from the low velocity (large deflection) side of the probability curve, scintillations will be missing owing to loss of charge in the mica, the numbers missing being greater the smaller the velocity. Now these particles which lose a charge will have a velocity equal to the doubly charged particles which passed through a slit and consequently they will not reach the screen. Thus, a band of scintillations produced by singly charged particles would also be expected, but the maximum number should be at a velocity smaller than that at which the doubly charged band is a maximum.

Fig. 3 shows one of the curves obtained, the number of scintillations observed per minute being plotted against the deflection. Two maxima were obtained which obviously corresponded to singly and doubly charged particles. The velocity corresponding to the maxima were $0 \cdot 23\ V_0$ and $0 \cdot 31\ V_0$ respectively. This is in accordance with the conclusion arrived at above, that the velocity corresponding to the maximum of the singly charged particles must be less than that corresponding to the maximum of the doubly charged particles. As it was shown by Rutherford* the ratio of the number of singly charged particles

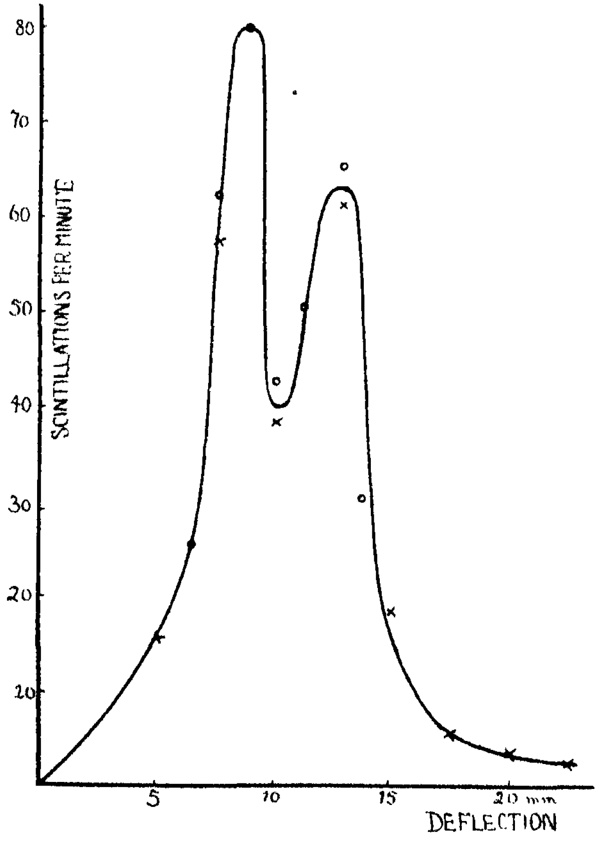

Fig. 3.

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* *Loc. cit.*

to the number of doubly charged particles increases as the velocity diminishes. In fig. 3 this ratio is seen to be already more than unity. When the velocity of the α-particles falling on the screen was further reduced (by altering the field and the setting of the holder) the doubly charged particles eventually disappeared, and only one maximum was obtained, as is shown in fig. 4.

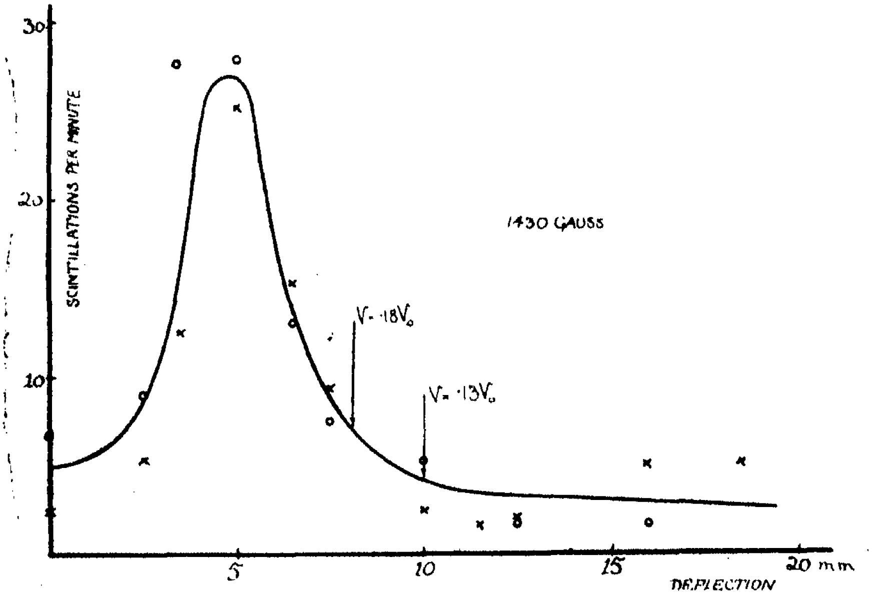

FIG. 4.

On further reduction of the velocity a phenomenon similar to that observed by Marsden and Taylor* occurred. The velocity corresponding to the maximum remained practically unchanged, while the number of the α-particles diminished. A curve for such very low velocities is given in fig. 5. The results obtained in the previous chapter throw some light on this phenomenon, as will be shown later.

The velocity of the slowest α-particles capable of producing a visible scintillation was determined from fig. 5, it being taken that the smallest velocity at which the number of α-particles observed is just greater than the background produced by scattering and contamination. This limit is marked by a dotted line and corresponds to a velocity $= 0 \cdot 13\ V_0$. In both the experimental curves shown, points marked differently correspond to two series of counts, one travelling from top to bottom of the screen, and the other from bottom to top.

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* *Loc. cit.*

Taking for the limit the value $V = 0 \cdot 13\ V_0$, then the energy of the $\alpha$-particle will be 0·017 of the original energy of the $\alpha$-particle.

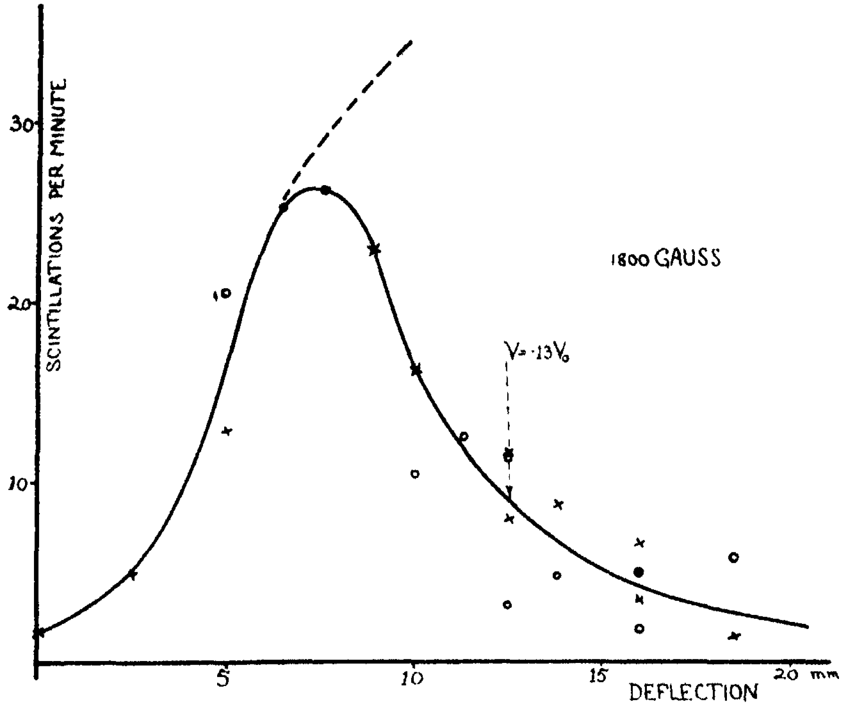

Fig. 5.

In order to assist the visualisation of this result, let us calculate the energy entering the eye from such a scintillation in terms of quanta of green light ($\lambda = 0 \cdot 505\ \mu$). Supposing the efficiency of the process of scintillation formation to be independent of the energy of the $\alpha$-particles, then if E is the initial energy of an $\alpha$-particle from radium C $= 1 \cdot 3 \,.\, 10^{-5}$ erg and if $\beta$ is the efficiency $= 0 \cdot 13$ (Güntz 112 zinc-sulphide),

$\gamma$ is the transmissivity of the microscope $= 0 \cdot 8$.

$q$ is the energy in a quanta of green light $\lambda = 0 \cdot 505\ \mu = 3 \cdot 9 \,.\, 10^{-12}$.

$f$ is the fraction of light from the scintillation entering the eye objective, which for N.A. $= 0 \cdot 45$ is $5 \cdot 3 \,.\, 10^{-2}$.

$N = E \times 0 \cdot 017 \,.\, \beta \,.\, \gamma \,.\, f/q = 290$ quanta ($\lambda = 0 \cdot 505\ \mu$).

### C.—Summary of Experimental Results.

(1) The minimum radiation entering the eye in short flashes of duration less than 1/100 second which produced a perceptible sensation was evaluated in

terms of green light ($\lambda = 0 \cdot 505\ \mu$) and was found to be $6 \cdot 6 . 10^{-11}$ ergs, or approximately 17 quanta.

(2) The radiant and luminous efficiencies of the process of scintillation formation in various zinc-sulphides were found to be of the order of 20 per cent. and 10 per cent. respectively, but varying slightly among the different preparations.

(3) The velocity of the slowest $\alpha$-particles which produce scintillations observable in a microscope of numerical aperture 0·45 and magnification 50 was found to 0·13 of the initial velocity of radium C $\alpha$-particles, *i.e.*, $2 \cdot 7 . 10^8$ cm./sec. In this case, using the value obtained for the efficiency of the zinc-sulphide used, the energy entering the eye, from a single scintillation evaluated as green light, has the value of 300 quanta ($\lambda = 0 \cdot 505\ \mu$).

(4) When scintillations produced by $\alpha$-particles of 2·7 cm. range are observed with a microscope of magnification 50 and of variable numerical aperture, the scintillations become invisible when the numerical aperture is reduced below 0·08. With this value of the numerical aperture the energy entering the eye from a single scintillation evaluated as green light ($\lambda = 0 \cdot 505\ \mu$) is 290 quanta.

When scintillations are observed with the naked eye placed at varying distance from the zinc-sulphide screen, the scintillations become invisible when the eye receives less than 30 quanta per scintillation.

## D.—DISCUSSION.

### *Interpretation of Results Obtained.*

In order that scintillations shall be perceived by the naked eye an amount of luminous energy equivalent to 30 quanta of green light must enter the eye from each scintillation. When short flashes are occurring regularly both in time and position, only 17 quanta must enter the eye per flash in order that they may be visible. The difference—a factor of 2—is not surprising, when it is remembered that certain parts of the retina are much more sensitive than others, and the eye can be adjusted to receive regularly occurring flashes on the most sensitive parts of the retina.

The figures obtained for the energy entering the eye from a barely visible scintillation from the observation of slow $\alpha$-particles and from the observation of bright scintillations and small numerical aperture are in good agreement—about 300 quanta.

In the first of these two cases a slow $\alpha$-particle only penetrates the surface layers of the crystal, while in the second case a fast $\alpha$-particle travels to a considerable depth in the crystal. The agreement between these two cases might be taken as a proof that the efficiency of the process of scintillation formation is the same in both cases.

The values obtained in these two cases are, however, several times larger than those obtained with the naked eye.

The reason for this divergence lies apparently in the optical properties of the zinc-sulphide crystals. The shape of the crystals is very irregular and, consequently, when an $\alpha$-particle shoots through one of them, the light produced is reflected and refracted from the various surfaces and an image is formed in the microscope not of the actual path of the $\alpha$-particle, but of the illuminated crystal itself. This can easily be seen by examining a zinc-sulphide screen bombarded by $\alpha$-particles with a microscope of magnification 800. When an $\alpha$-particle strikes a crystal the whole, or a large part, of the crystal appears to light up. When the crystals are more regular it is possible to see the actual paths of the $\alpha$-particles in the crystal. Geiger,[*] using magnification 450, was able to see $\alpha$-particle tracks in Willemite. The authors were able to observe the tracks in a diamond crystal, using a magnification 1200, when the tracks appeared as perfectly definite sharp lines.

It is, therefore, quite reasonable to suppose that the "size" of a scintillation is the same as the size of a crystal of zinc-sulphide. Examination of the crystals under a high-power microscope shows that for Güntz 112 zinc-sulphide the dimensions of the crystals vary between 10 $\mu$ and 50 $\mu$. But the majority of the crystals appear to have an average diameter of 25 $\mu$. Consequently, the size of the image on the retina of a crystal viewed with the naked eye placed at a distance of 25 cm. will be about 2·2 $\mu$. When a microscope magnifying 50 times is used the size of the retinal image will be about 110 $\mu$.

The dimensions of the retinal image of the crystal when observed with the naked eye are of the same order as those of the retinal image of the flashing point used in the determination of "the limit of vision" (6 $\mu$). Between these two cases we find a good agreement for the value of the limit. The question remains whether the increased size of the retinal image when a microscope is used is sufficient to account for the increased value of the limit obtained.

Information concerning the relation between the size of retinal image of the stimulus and the corresponding "limit of vision" can be obtained from Prentice Reeves'[†] work.

Although the experiments of Reeves were performed with steady sources of light, it seems improbable that the influence of the size of retinal image on the limit of vision will be different in the cases of short flashes and steady light.

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[*] 'Z. Physik,' vol. 8, p. 191 (1921).

[†] 'Astrophys. J.,' vol. 47, p. 141 (1918).

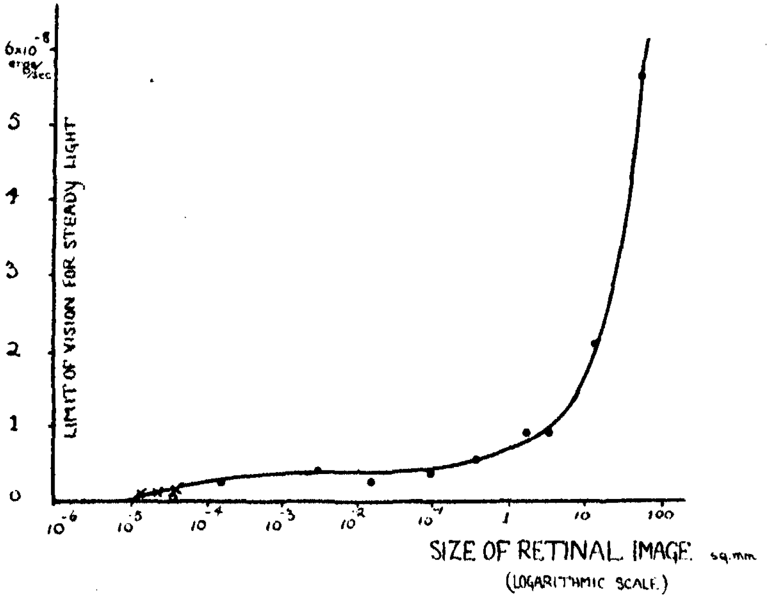

Fig. 6.

Reeves' results are shown in fig. 6 where the value of the limit in ergs per second are plotted against size of retinal image, logarithmic scale being used. Three points taken from the work of M. Buisson* are also shown together with the value of the limit obtained in the first chapter of this work.

The curve shows that the minimum radiation visually perceptible increases gradually as the size of retinal image increases until the neighbourhood of $10^{-3}$ mm.$^2$ is reached, the limit then remains constant as the size of image increases to 0·1 sq. mm. and then begins to rise again.

The size of retinal image of scintillations viewed with the naked eye and microscope are $5 \times 10^{-5}$ sq. mm. and $10^{-2}$ sq. mm. respectively. From Reeves' and Buisson's results it is seen that the limit increases about six times in this interval. A check on this increase was made with flashes instead of steady light and an increase of four times was found, which is somewhat less than the factor of 10 obtained between the values of the limit calculated from the observation of scintillations with the naked eye and through the microscope.

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* 'Astrophys. J.,' vol. 46, p. 296 (1917).

If this interpretation of the figures obtained is correct, the best optical system for counting would theoretically be one of large numerical aperture, but of magnification unity or very little more. Small magnification would, however, necessitate the use of a large area of zinc-sulphide screen, since for the comfort and precision of counting a large field of view is desirable. Hence the application of low magnification can only be of practical value in very special cases.

From the results given above some information can be obtained as to the minimum velocity of the $\alpha$-particles. whose numbers can be reliably determined by counting the scintillations they produce. From fig. 1 it can be seen that the number of scintillations observed begins to drop off when the energy entering the eye is less than 1200 quanta ($\lambda = 0 \cdot 505\ \mu$).

From this result it can be readily calculated that $\alpha$-particles to be reliably counted, with a microscope of N.A. 0·45 and magnification 50, should have a velocity not less than $0 \cdot 25\ V_0$ where $V_0$ is the velocity of the $\alpha$-particles from radium C. This velocity corresponds to a residual range in air of 3·5 mm.

It is interesting to note that this figure coincides with that given by Rutherford* for the slowest $\alpha$-particles which can be conveniently counted. The limit of visibility which is given here as $0 \cdot 13\ V_0$ is also very nearly equal to the figure given by Rutherford for "difficult counting," namely, $0 \cdot 15\ V_0$.

When a microscope of numerical aperture 0·45 is used the energy entering the eye from scintillations produced by $\alpha$-particles of velocities between $0 \cdot 25\ V_0$ and $0 \cdot 13\ V_0$ has a value between 1200 and 300 quanta. Thus, according to the curve, fig. 14, not all the scintillations produced will be observable.

If these results are applied to those obtained in Section B an explanation may be given for the phenomenon observed by Marsden and Taylor, and also by the authors, in which the maximum of the number of $\alpha$-particles deflected in a magnetic field became immovable after a certain limit was reached. If we suppose that the actual distribution of the $\alpha$-particles on the screen has a maximum at $0 \cdot 15\ V_0$, the distribution of scintillations observed will be quite different. The value of the maximum will be reduced, as only 25 per cent. of the scintillations will be seen (when observed by a microscope of N.A. 0·45), and the maximum of the number observed will be removed to the region of larger velocities. This may be the reason why the maximum of the scintillations observed could not be replaced towards the region of smaller velocities.

If the number of quanta entering the eye from each scintillation is known, then the true number of $\alpha$-particles striking the screen can be obtained from the number observed, with the help of the curve in fig. 1. The dotted curve in fig. 5 shows the actual number of α-particles obtained in this way. This method of correcting the number of faint scintillations observed can only be applied when the scintillations under observation are produced by a homogeneous beam of α-particles. This can be readily seen by comparing a curve showing how the number of scintillations produced by a beam of α-particles falls off as their range is reduced, with the curve in fig. 1. The difference between these two curves seems, however, to be of the order that would be expected from the known straggling of the α-particles.

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* 'Phil. Mag.,' vol. 47, p. 282 (1924).

### *Scintillations produced by β-particles.*

It is well known that β-particles produce a strong fluorescence in zinc-sulphide. Since, however, the fluorescence produced by β-rays is of quite a different appearance to the scintillations produced by α-particles the presence of β-rays does not in general prevent the counting of scintillations due to α-particles, though it may introduce a disturbing influence owing to the brightness of the zinc-sulphide screen, and the fluctuating character of the fluorescence, due to the fluctuations in the number of β-particles falling on different parts of the screen.

The reason why β-particles produce a general fluorescence rather than scintillations is, of course, due to the fact that a β-particle in passing through an average ZnS crystal does not lose sufficient energy to produce a visible scintillation. It has been known in this laboratory for some time, however, that under certain conditions very faint scintillations can be observed when only β-particles are allowed to fall on a ZnS screen. This observation can be simply explained and shown to agree with the data given in this paper.

The crystals of ZnS had an average dimension of about 25 μ. It is difficult to estimate how much energy would be lost by a β-particle in passing through such a crystal, but we may take as a rough approximation for average β-rays, such as those of RaE, a value of 14,000 electron volts. Assuming the same luminous efficiency for β-rays as was found for α-rays, the luminous energy radiated by a ZnS crystal when a β-particle passes through it will be about 660 quanta of green light. If a microscope of 0·65 N.A. is used for observation, the amount of energy which enters the eye will be about 80 quanta. It has been shown that about 300 quanta are required in order that a scintillation should be visible through a microscope, and therefore the scintillation due to a single β-particle cannot be detected. If, however, several β-particles struck the same ZnS crystal during the period of relaxation of the eye sufficient luminous energy may be released to give a visible scintillation. If the total number of β-particles falling on the screen is small the possibility of this event is small. If the number of β-rays falling on the screen is large the required event may occur frequently, but the general fluorescence of the screen may be so intense as to prevent the observation of the scintillations. There should, therefore, be a certain range of density of the β-radiation which is most favourable to the observation of the scintillations. This corresponds to our experience and explains why β-particle scintillations are not generally observed.

Let $n_0$ be the average number of β-particles falling on each crystal per second, and let $n$ be the number which must strike a single crystal during a period of relaxation of the eye (1/10 second, say) in order that a scintillation may be observed. Then the probability that a scintillation will be produced in any given crystal during 1/10 second will be merely the probability of more than $n$ occurrences when the mean number of occurrences is $n_0/10$. Thus, if the number of crystals in the field of view of the microscope be N, the number of scintillations per minute will be

$$\sum_{n=n}^{n=\infty} \frac{\left(\frac{n_0}{10}\right)^n}{n\,!} e^{-\frac{n_0}{10}} \,.\, 600\mathrm{N} = \mathrm{P}.$$

No very definite idea can be obtained from this expression as to the intensity of β-ray bombardment necessary for the scintillations to be most clearly seen, without precise knowledge as to how the visibility of scintillations varies with the intensity of the general illumination of the screen. It can be expected, however, that the best conditions will be realised when $n_0$ is considerably less than $n$, but sufficient to give P a value which is reasonably countable.

A test of the above reasoning can, however, be made by adjusting the distance of a β-ray source from a zinc-sulphide screen until the optimum conditions are obtained, estimating the number of scintillations observable per minute, calculating the value of $n$ by substituting for P in the above expression and seeing if the value obtained agrees with the ratio of 300 quanta, the minimum visible, to 80 quanta, the maximum entering the eye from a single β-particle striking a ZnS crystal.

The following experiment was performed. A ZnS screen was bombarded by β-particles from a source of radium E and observed with a microscope of N.A. 0·65. Sheets of mica of total air equivalent of 16 cm. were placed over the source to prevent the production of scintillations by H-particles.

When the source was placed at a distance of 0·5 cm. the screen glowed strongly, but at a distance of 1·0 cm. about 100 very faint scintillations per minute could be observed. Further displacement of the source produced a rapid decrease in the number of scintillations and finally a complete disappearance.

The β-ray activity of the source was measured and found to be 0·3 millicurie. The α-ray activity of the source was also measured and found to be 0·1 millicurie, with the mica sheets removed.

The field of view of the microscope was 7 sq. mm., the number of crystals on this area being about 7000. From these data $n_0$ has a value of about 10, and substituting $P = 100$ in the above expression, we find that $n$ has a value of about 7. This is in reasonable agreement with the ratio 300/80 obtained in the foregoing as a minimum value of $n$.

## F.—MECHANISM OF SCINTILLATION PROCESS.

Pure zinc-sulphides, as it is well known, do not scintillate when bombarded by α-particles, nor do they fluoresce under the action of light. In order to "sensitise" the zinc-sulphide to the action of these factors an insertion of minute quantities of impurities, such as copper, manganese or some other metal, is necessary. The amounts of impurities in commercially-used zinc-sulphides, or those employed for scintillation counting, are of the order of 0·01 per cent. It is indeed very surprising that such a small amount of foreign matter produces such a capital change in the properties of the crystal.

Lenard* supposed that the foreign atoms bound in the crystal lattice produced local disturbances which are responsible for the observed change of properties. Very little, however, is known as to the nature of these active centres or the kind of disturbance they produce in the crystal lattice.

The high values obtained for the radiant efficiencies oblige us to adopt a rather definite picture of the mechanism of scintillation production.† It is quite obvious that if α is the efficiency, at least the part α of the whole volume of the zinc-sulphide crystals must be occupied by active centres, since the rate at which the α-particle loses energy cannot be appreciably different in the active and inactive parts of the crystal. We must assume, therefore, unless we suppose the efficiency of transformation of the energy of the α-particle into light is considerably greater than 100 per cent. in the active parts of the crystal that practically all the volume of the crystal is effective in producing scintillations.

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* 'Handbuch der Experimental Physik,' vol. 23, p. 89.

† It may be interesting to note here that the values obtained by H. W. Ernst ('Ann. Physik,' vol. 82, p. 1051 (1927)) for the efficiency of the transformation of the energy of cathode rays into radiant energy in certain fluorescing substances were of the order of 10 per cent.

The disturbances caused by the impurities are, therefore, apparently spread all through the volume of the crystal, forming a kind of network of slight strains which allow the molecules of the crystal to respond to excitation by $\alpha$-particles in a way which is impossible in the normal crystal.

This suggestion is in agreement with the conclusion arrived at by Rutherford in his " Theory of luminosity produced in certain substances by $\alpha$-rays."*

By analysing the experimental data concerning the decay of luminosity under prolonged bombardment obtained by Marsden,† Rutherford came to the conclusion that the dimensions of the " active centres " are of molecular order. The suggestion then that the whole crystal is active, *i.e.*, all the molecules are active, seems to be consistent with Rutherford's theory.

In order to explain the rate of decay observed by Marsden, Rutherford assumed that the radius of action of the $\alpha$-particle, *i.e.*, the diameter of the cylinder drawn around the $\alpha$-particle in which all the active centres were destroyed, is of the order of $1 \cdot 3 \times 10^{-7}$ cm. in zinc-sulphide. From the point of view offered here this will mean that all the disturbances or strains produced in the crystal by impurities are destroyed in a cylinder of this diameter drawn around the path of the $\alpha$-particle.

## *Summary.*

The question of how the amount of light entering the eye from an individual scintillation affects the number of scintillations observed was investigated. The results were not in agreement with those obtained by B. Karlik.

Scintillations were observed with the naked eye, and it was found that a smaller fraction of the light from a scintillation produces a visual sensation when the eye is unaided, than when a microscope is used. A partial explanation was given in view of the difference in the sizes of the retinal images in the two cases.

The velocity of the slowest $\alpha$-particle capable of producing a visible scintillation was measured. The value obtained agreed very closely with that given by Rutherford.

The experimental results obtained in the three parts of the paper were summarised and discussed.

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* 'Roy. Soc. Proc.,' A, vol. 83, p. 561 (1908).

† 'Roy. Soc. Proc.,' A, vol. 83, p. 548 (1908).

An explanation was given of the formation of very faint scintillations when β-rays fall on a zinc-sulphide screen in suitable numbers.

The high value obtained for the efficiency of the scintillation process in Part II of this paper was discussed in connection with the mechanism of scintillation production.

The authors would like to express their gratitude to Sir Ernest Rutherford for the interest he has taken during the progress of this work. They would also like to thank Dr. J. Chadwick for suggesting the problem and for many helpful suggestions and criticisms. They are further indebted to Mr. G. R. Crowe for the preparation of radioactive sources.

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## *The Tensorial Form of Dirac's Wave Equations.*

By G. TEMPLE, Ph.D., Imperial College, 1851 Exhibition Research Student.

(Communicated by S. Chapman, F.R.S.—Received November 13, 1928.)

§ 1. It is an admitted fact that Dirac's wave functions* are not the components of a tensor and that his wave equations are not in tensorial form. It is contended here that therefore his theory cannot be upheld without abandoning the theory of relativity. The object of this paper is to formulate a system of wave equations which shall possess the same advantages as Dirac's equations and which shall be tensorial in form in accordance with the general theory of relativity.

Since a tensor is a set of numbers representing in some system of co-ordinates some physical entity, it follows that to every transformation (S) of the co-ordinate system there must correspond one and only one transformation (T) of the components of the tensor. Moreover the fundamental principle of all relativistic theories is that the product of any pair, $T_1$, $T_2$, of the transformations (T) must correspond to the product of the corresponding pair, $S_1$, $S_2$, of the transformations (S). This may be briefly expressed by saying that the groups (S) and (T) are similar.†

Darwin‡ has proposed a law of transformation for Dirac's four wave functions. By means of his equations and proper limitations upon the values of the parameters a definite transformation (T) of the wave functions may be associated with every transformation (S) of the general Lorentz group. But it is evident upon an inspection of his equations that the groups (T) and (S) are not similar. In example, two half-turns about the same axis yield the identical transformation in the (S) group. But the product of the corresponding (T) transformations fails to yield the identical transformation. Hence wave functions obeying Darwin's law of transformation would not be tensors, and, unless relativity is to be discarded, they could not have any physical significance.

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* 'Roy. Soc. Proc.,' A, vol. 117, p. 610, and vol. 118, p. 351 (1928).

† Ricci and Levi-Civita, 'Math. Ann.,' vol. 54, p. 128 (1901).

‡ 'Roy. Soc. Proc.,' A, vol. 118, p. 654 (1928).

Happily it is possible to replace Dirac's equations by a tensor equation satisfied by a wave tensor, $\phi_\mu$, of the first rank. The components of this tensor are formally distinct from the wave functions of Dirac, but the wave equations fulfil the two conditions laid down as the foundation of Dirac's investigation, namely, they are linear differential equations of the first order and they yield the Schrödinger-Gordon wave equation when there is no electromagnetic field.

## § 2. *The Characteristic Tensor.*

Gordon* has shown that Dirac's wave equations may be written in the symmetrical form,

$$\sum_{\nu=1}^{4}\left\{i\lambda\kappa_\nu + \frac{\partial}{\partial x^\nu}\right\}(\gamma^\nu\phi) = i\omega\,(\phi),$$

where $\omega = 2\pi mc/h$, $\lambda = 2\pi e/hc$, $\kappa_\nu$ is the covariant electromagnetic potential tensor, $(\phi)$ denotes an ordered set of wave functions $(\phi_1, \phi_2, \phi_3, \phi_4)$, while $(\gamma^\nu\phi)$ denotes the set of four functions obtained by operating on $(\phi)$ with the linear substitution defined by the matrix $\gamma^\nu$. The form of this equation suggests that the wave functions should be taken as the components of a covariant tensor of the first rank. In rewriting the wave equations in tensorial form we denote the covariant derivative of $\phi_\mu$ with respect to $x^\nu$ by the symbol, $(\phi_\mu)_\nu$, and we introduce the characteristic tensor, $\gamma^{\mu\nu}{}_\alpha$, which determines the constituents of the four matrices, $\gamma^\nu$. The wave equations may then be rewritten as

$$i\omega\phi_\alpha = \gamma^{\mu\nu}{}_\alpha\,.\,(\phi_\mu)_\nu + i\lambda\gamma^{\mu\nu}{}_\alpha\,.\,\phi_\mu\kappa_\nu. \tag{A}$$

We shall assume that the matrices are Hermitian, so that the contravariant tensor, $\gamma^{\mu\nu\alpha}$, associated with the characteristic tensor, satisfies the relations,

$$\gamma^{\mu\nu\alpha} = \bar{\gamma}^{\alpha\nu\mu}, \tag{B}$$

where $\bar{\gamma}$ denotes the complex number conjugate to $\gamma$.

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* Gordon, 'Z. Physik,' vol. 50, p. 630 (1928).

To determine what further restrictions must be placed upon the characteristic tensor it is sufficient to consider the wave equations for a free electron, namely,

$$i\omega\phi_\alpha = \gamma^{\mu\nu}{}_\alpha \cdot (\phi_\mu)_\nu.$$

We require these equations to lead to the result

$$-\omega^2\phi_\alpha = g^{\tau\nu}(\phi_\alpha)_{\tau\nu},$$

where $g^{\tau\nu}$ is the fundamental contravariant tensor of the metrical manifold. This implies that the characteristic tensor satisfies the relations,

$$\gamma^{\mu\nu}{}_\alpha \cdot \gamma^{\sigma\tau}{}_\mu + \gamma^{\mu\tau}{}_\alpha \cdot \gamma^{\sigma\nu}{}_\mu = 2g^{\tau\nu}g_\alpha{}^\sigma, \tag{C}$$

and

$$\gamma^{\mu\nu}{}_\alpha \cdot (\gamma^{\sigma\tau}{}_\mu)_\nu = 0. \tag{D}$$

In deducing the wave equations from a Lagrangian function (§ 3) and in obtaining the equation of continuity satisfied by the stream tensor (§ 5), it is necessary to add the further condition,

$$(\gamma^{\mu\nu}{}_\alpha)_\nu = 0. \tag{E}$$

The four conditions, B, C, D, E, will be referred to as the "characteristic equations."

If we introduce the fourth rank tensor, defined by the equation

$$\beta_\alpha{}^{\sigma\tau\nu} = \tfrac{1}{2}(\gamma^{\mu\nu}{}_\alpha \cdot \gamma^{\sigma\tau}{}_\mu - \gamma^{\mu\tau}{}_\alpha \cdot \gamma^{\sigma\nu}{}_\mu), \tag{F}$$

we may write

$$\left.\begin{aligned} \gamma^{\mu\nu}{}_\alpha \cdot \gamma^{\sigma\tau}{}_\mu &= g^{\tau\nu}g_\alpha{}^\sigma + \beta_\alpha{}^{\sigma\tau\nu} \\ \text{and}\quad \gamma^{\mu\tau}{}_\alpha \cdot \gamma^{\sigma\nu}{}_\mu &= g^{\tau\nu}g_\alpha{}^\sigma - \beta_\alpha{}^{\sigma\tau\nu} \end{aligned}\right\} \tag{G}$$

We notice that $\beta_\alpha{}^{\sigma\tau\nu}$ is antisymmetrical in $\tau$ and $\nu$, and that, in virtue of equations (D) and (E), it satisfies the equation

$$(\beta_\alpha{}^{\sigma\tau\nu})_\tau = 0. \tag{H}$$

## § 3. *The Lagrangian Function.*

Guided by the form of the wave equations (A) we take the Lagrangian function to be

$$\mathfrak{L} = (-g)^{\frac{1}{2}}\,\mathrm{L},$$

where

$$\mathrm{L} = \omega\phi_\alpha\bar{\phi}^\alpha - \lambda\gamma^{\mu\nu}{}_\alpha\phi_\mu\,\bar{\phi}^\alpha\kappa_\nu + \tfrac{1}{2}i\,\{\gamma^{\mu\nu}{}_\alpha(\phi_\mu)_\nu\,\bar{\phi}^\alpha - \bar{\gamma}_\alpha{}^{\nu\mu}\,\phi_\mu\,(\bar{\phi}^\alpha)_\nu\}.$$

If we denote the three-index symbols of the second species by $\Gamma_{\sigma\nu}{}^\alpha$, the covariant derivative in L is

$$(\bar{\phi}^\alpha)_\nu = \frac{\partial\bar{\phi}^\alpha}{\partial x^\nu} + \Gamma_{\sigma\nu}{}^\alpha\,\bar{\phi}^\sigma.$$

We find that

$$\partial \mathfrak{L}/\partial \bar{\phi}^a = (-g)^{\frac{1}{2}}\{L_a - \tfrac{1}{2}i\bar{\gamma}_\sigma{}^{\nu\mu} \,.\, \phi_\mu \Gamma_{a\nu}{}^\sigma\},$$

where

$$L_a = \omega\phi_a + \gamma^{\mu\nu}{}_a \,.\, \{(\tfrac{1}{2}i\phi_\mu)_\nu - \lambda\phi_\mu\kappa_\nu\};$$

and

$$\partial \mathfrak{L}\Big/\partial\left(\frac{\partial \bar{\phi}^a}{\partial x^\nu}\right) = (-g)^{\frac{1}{2}} L_a{}^\nu,$$

where

$$L_a{}^\nu = -\tfrac{1}{2}i\bar{\gamma}_a{}^{\nu\mu}\phi_\mu = -\tfrac{1}{2}i\gamma^{\mu\nu}{}_a\phi_\mu,$$

by equation (B). Hence the Lagrangian equations may be written in the tensorial form,

$$(L_a{}^\tau)_\tau \quad L_a,$$

whence

$$-\omega\phi_a = \gamma^{\mu\nu}{}_a \,.\, \{(i\phi_\mu)_\nu - \lambda\phi_\mu\kappa_\nu\},$$

which is equivalent to (A).

## § 4. *The Wave Equations.*

In deducing the second order wave equations we introduce the electromagnetic tensor of the second rank,

$$F_{\tau\nu} = (\kappa_\tau)_\nu - (\kappa_\nu)_\tau,$$

and we make use of the relation,

$$g^{\tau\nu}(\kappa_\tau)_\nu = (\kappa^\nu)_\nu = 0.$$

Then, if we substitute

$$i\omega\phi_\mu = \gamma^{\sigma\tau}{}_\mu\{(\phi_\sigma)_\tau + i\lambda\phi_\sigma\kappa_\tau\}$$

in the equation

$$i\omega\phi_a = \gamma^{\mu\nu}{}_a\{(\phi_\mu)_\nu + i\lambda\phi_\mu\kappa_\nu\},$$

and make use of the characteristic equations, we obtain finally the second order equation,

$$-\omega^2\phi_a = g^{\tau\nu}(\phi_a)_{\tau\nu} + 2i\lambda g^{\tau\nu}\kappa_\tau(\phi_a)_\nu - \lambda^2 g^{\tau\nu}\kappa_\tau\kappa_\nu\phi_a + \tfrac{1}{2}i\lambda\beta_a{}^{\sigma\tau\nu}F_{\tau\nu}\phi_\sigma. \quad \text{(I)}$$

## § 5. *The Stream Tensor.*

The stream tensor, which determined the charge and current density, may be defined as

$$j^\nu = -\partial L/\lambda\,\partial\kappa_\nu = \bar{\phi}^a\gamma^{\mu\nu}{}_a\phi_\mu. \quad \text{(J)}$$

We proceed to establish the equation of continuity.

From the definition of $j^\nu$ and from equation (E) we find that

$$\begin{aligned}(j^\nu)_\nu - \bar{\phi}^\alpha\gamma^{\mu\nu}{}_\alpha\,.\,(\phi_\mu)_\nu &= (\bar{\phi}_\sigma)_\nu\gamma^{\mu\nu\sigma}.\ \phi_\mu \\ &= (\bar{\phi}_\sigma)_\nu\bar{\gamma}^{\sigma\nu\mu}.\ \phi_\mu \text{ (from equation (B) )} \\ &= (\bar{\phi}_\alpha)_\nu\,\bar{\gamma}^{\alpha\nu}{}_\mu\,.\,\phi^\mu.\end{aligned}$$

Therefore, from the wave equation (A) and its conjugate,

$$\begin{aligned}(j^\nu)_\nu &= \bar{\phi}^\alpha\,(i\omega\phi_\alpha - i\lambda\gamma^{\mu\nu}{}_\alpha\phi_\mu\kappa_\nu) \\ &\qquad + \phi^\mu\,(-\,i\omega\bar{\phi}_\mu + i\lambda\bar{\gamma}^{\alpha\nu}{}_\mu\,.\,\bar{\phi}_\alpha\kappa_\nu) \\ &= i\lambda\,(\gamma^{\alpha\nu\mu} - \gamma^{\mu\nu\alpha})\,\phi_\mu\bar{\phi}_\alpha\kappa_\nu = 0 \quad \text{(by equation (B) ).}\end{aligned}$$

Hence the stream tensor satisfies the equation of continuity,

$$(j^\nu)_\nu = 0. \tag{K}$$

## § 6. *The Magnetisation and Polarisation Tensor.*

Following the method used by Gordon (*loc. cit.*) we now analyse the total stream tensor into two parts, one due to convection, the other to magnetisation and polarisation.

By the definition of the stream tensor,

$$\begin{aligned}2i\omega j^\nu &= i\omega\bar{\phi}_\mu\gamma^{\sigma\nu\mu}\phi_\sigma + \bar{\phi}_\alpha\gamma^{\mu\nu\alpha}i\omega\phi_\mu \\ &= -\,\gamma^{\sigma\nu\mu}\,.\,\bar{\gamma}^{\alpha\tau}{}_\mu\,\{(\bar{\phi}_\alpha)_\tau - i\lambda\bar{\phi}_\alpha\kappa_\tau\}\,\phi_\sigma \\ &\qquad + \gamma^{\mu\nu\alpha}\gamma^{\sigma\tau}{}_\mu\,\{(\phi_\sigma)_\tau + i\lambda\phi_\sigma\kappa_\tau\}\,\bar{\phi}_\alpha \quad \text{(by equation (A) )} \\ &= -\,(g^{\tau\nu}g_\alpha{}^\sigma - \beta_\alpha{}^{\sigma\tau\nu})\,\{(\bar{\phi}^\alpha)_\tau - i\lambda\bar{\phi}^\alpha\kappa_\tau\}\,\phi_\sigma \\ &\qquad + (g^{\tau\nu}g_\alpha{}^\sigma + \beta_\alpha{}^{\sigma\tau\nu})\,\{(\phi_\sigma)_\tau + i\lambda\phi_\sigma\kappa_\tau\}\,\bar{\phi}^\alpha \quad \text{(by equations (B) and (G) ).}\end{aligned}$$

Hence, having regard to equation (H), we may write

$$2i\omega j^\nu = s^\nu + (\mathrm{M}^{\tau\nu})_\tau, \tag{L}$$

where

$$s^\nu = g^{\tau\nu}\,\{\bar{\phi}^\sigma\,(\phi_\sigma)_\tau - (\bar{\phi}^\sigma)_\tau\,\phi_\sigma + 2i\lambda\kappa^\nu\phi_\alpha\bar{\phi}^\alpha\},$$

and

$$\mathrm{M}^{\tau\nu} = \beta_\alpha{}^{\sigma\tau\nu}\bar{\phi}^\alpha\phi_\sigma. \tag{M}$$

The latter is the required tensor giving the polarisation and magnetisation.*

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* See also Darwin, 'Roy. Soc. Proc.,' A, vol. 120, p. 621 (1928).

## § 7. *The Quadratic Invariants.*

The simplest real quadratic invariants are

$$\Delta_1 = \phi_a \bar{\phi}^a, \quad \Delta_2 = \phi_a \phi^a + \bar{\phi}_a \bar{\phi}^a$$

and

$$\left. \begin{array}{l} \\ \Delta_3 = i\,(\phi_a \phi^a - \bar{\phi}_a \bar{\phi}^a), \end{array} \right\} \qquad \text{(N)}$$

and these are all necessarily independent.

To calculate the invariant $j^\nu j_\nu$ we express the stream tensor in four equivalent forms, as

$$j^\nu = \bar{\phi}^\alpha \gamma^{\mu\nu}{}_\alpha \phi_\mu = \bar{\phi}^\mu \gamma^{\sigma\nu}{}_\mu \phi_\sigma,$$

$$j^\tau = \bar{\phi}^\mu \gamma^{\sigma\tau}{}_\mu \phi_\sigma = \bar{\phi}^\alpha \gamma^{\mu\tau}{}_\alpha \phi_\mu.$$

Then

$$2j^\nu j^\tau = (\gamma^{\mu\nu}{}_\alpha \gamma^{\sigma\tau}{}_\mu + \gamma^{\mu\tau}{}_\alpha \gamma^{\sigma\nu}{}_\mu) \bar{\phi}^\alpha \phi_\sigma \bar{\phi}^\mu \phi_\mu,$$

$$= 2g^{\tau\nu} \bar{\phi}^\alpha \phi_\alpha \phi^\mu \phi_\mu \quad \text{(by equation (C)) .}$$

Therefore

$$j^\nu j_\nu = 4\,\Delta_1{}^2. \qquad \text{(O)}$$

I have not been able to express the invariant $M^{\tau\nu} M_{\tau\nu}$ in terms of the quadratic invariants given above. Possibly Darwin's result* depends upon the degenerate form of the characteristic tensor used by Dirac.

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* *Loc. cit.*

# *The Charge of an Electron.*

By A. S. Eddington, F.R.S.

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1. It is well known that the ratio of $hc$ to $e^2$ is a pure number. The methods of macroscopic physics break up the number and scatter its factors, so that it strikes us as an artificial construction and its dimensionless character seems an irrelevant curiosity. But in the wave-theory of the interaction of electrons the number is kept intact. Since electric charge is only manifested in the interaction of at least two charges it is useless to consider a solitary electron. The most elementary appearance of $e$ in physics is in the wave-equation for two electrons (or an electron and proton); it there occurs in the combination $hc/2\pi e^2$ as the coefficient of certain terms.

The experimental value of $hc/2\pi e^2$ is 137·1 (Millikan's data). According to the theory proposed in this paper it should be the integer 136. Although the discrepancy is about three times the probable error attributed to the experimental value, I cannot persuade myself that the fault lies with the theory. The basis of my argument is the Exclusion Principle in the form given by Fermi and Dirac, viz., that the $\psi$ functions pertaining to a pair of electrons must be antisymmetrical. Combined with the theory of relativity, this appears to lead in an unforced manner to the value 136, viz., the number of symmetrical terms in an array of 16 rows and columns.

The chief steps of the deduction are: (1) The exclusion principle describes a mutual interaction of two electrons and it is unlikely that there is another independent kind of interaction; thus if correctly formulated it should comprise *all* their interaction, and hence determine the value of $e$. (2) Its most natural formulation does in fact lead to terms agreeing in form with those attributed to electric charge in the wave-equation. (3) The determination of the numerical coefficient of these terms depends on the number of degrees of freedom assigned to a system. If we are convinced that this is the correct line of attack, we shall probably be willing to accept the number of degrees of freedom suggested by the observational value, and contrive to arrange the phenomena in some kind of scheme which has the required number; this is a kind of exercise in which small mistakes are unlikely, that is to say, we might hesitate between 10 and 136 and 256, but not between 136 and 137. But in addition there converges towards this a result hinted at by the analysis in my former paper,* viz., that the " axes " identified as those of space and time in macroscopic theory are a selection from a set of 16; so that the full 16-space may be expected to appear in non-degenerate problems. If the problem is admitted to be one of 16-space it becomes fairly obvious that the appropriate number of degrees of freedom is 136. In fact the 136 degrees of freedom are merely the direct extension to a two-electron problem of the 16 " rotations " in the one-electron problem with which my former paper was largely occupied.

I am not very satisfied with the form in which I have to leave the conceptions towards which the theory leads. There is too much use of classical analogies—a method general enough a year ago, but which the quantum theory is gradually succeeding in replacing. But to make much improvement would, I think, lead into broader problems than I can well tackle, and it is perhaps not essential to the main purpose of this investigation. There are weak places in the deduction where the conceptions become too hazy to guide us definitely; but by that time we seem to be well in sight of the goal, and may have confidence to make the necessary jumps.

At the last moment I have learnt of a new determination of $e$ by Siegbahn which gives $4 \cdot 792 \,.\, 10^{-10}$. I understand that a higher value is obtained which would closely confirm the present theory: but there has not been time to verify this information.

2. In classical physics interaction between two particles indicates a difference in the behaviour of one according as the other is or is not present. In modern theory this is translated in terms of probabilities and interaction signifies a difference in our expectation of behaviour, so that the probabilities associated with one particle are modified by the presence of the other. There are two ways of treating this modification. The analysis in statistical problems consists in determining the way in which *a priori* probabilities are modified by special information and we may regard the modification due to interaction as *special* in this sense. Or we may incorporate the modification in our basis of probability and adopt a " new statistics."

Both alternatives have been used in describing the interaction of a pair of electrons. We introduce an electrical repulsion between them which is a special factor modifying the *a priori* probability of distribution. But we also assume that they obey a new statistics, viz., that of Fermi and Dirac. If these were two really independent kinds of interaction, it would nevertheless be desirable to express them in more comparable form. But it is reasonable to expect that if we examine one of them, say the Fermi-Dirac interaction, more carefully it will be found to contain the whole, and the interaction commonly ascribed to electric charge will be found to be merely the same thing in another guise.

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* 'Roy. Soc. Proc.,' A, vol. 121, p. 524 (1928).

It has probably not escaped notice that it can scarcely be necessary to postulate Fermi-Dirac statistics *in addition to* electric charge. The energy-term $e^2/r_{12}$ due to the charges introduces a singularity in the wave-equation for $r_{12} \rightarrow 0$, and this probably will prevent the equation from being satisfied by any finite symmetrical eigenfunctions; the antisymmetrical functions are saved because they give $\psi = 0$ for $r_{12} = 0$. The present paper pursues the converse idea—it can scarcely be necessary to postulate electric charge *in addition to* Fermi-Dirac statistics.

3. No physical phenomenon is affected by interchanging the identity of two electrons, any more than it is affected by rotating the axes of space and time. If therefore our formulæ exhibit the two electrons as though they had assigned identity, the convention is on the same footing as a special choice of space and time axes. It suggests itself that we should envisage a wider principle of relativity which admits, in addition to a rotation of space and time a "rotation" which will interchange the identity of two electrons. Now that an electron is no longer thought of as localised at a point such a conception is not ruled out by a barrier of discontinuity.

We have to consider a certain difficulty which arises in representing the position of a pair of electrons in space and time by 8 co-ordinates. Denote collectively the co-ordinates of two electrons $e$ and $e'$ by $q$ and $q'$ respectively, and consider a particular arrangement $q = \alpha$, $q' = \beta$. The two points in 8 dimensions $(\alpha, \beta)$ and $(\beta, \alpha)$ represent the same state of affairs, and by the exclusion principle the $\psi$ functions are related by the transformation

$$\psi(\alpha, \beta) = -\psi(\beta, \alpha). \tag{1}$$

It is not conducive to clearness of thought to continue to attribute two probability functions $\psi(\alpha, \beta)$ and $\psi(\beta, \alpha)$ to a given pair of electrons, and we should rather adopt a single function

$$\Psi = e^{i\theta}\psi(\alpha, \beta) = e^{i\theta}\psi(q, q'), \tag{2}$$

which can include them both. Here $\theta$ is a "co-ordinate" of the pair of electrons, which like other co-ordinates is relative to a frame of reference; but instead of being relative to particular axes of space and time it is relative to a particular assignment of identity to the two constituents of the pair. In particular when $\theta$ increases by $\pi$ the identity of the two electrons is interchanged. We regard the form (2) as the analytical expression of the exclusion principle. If, as usual, action is identified with the phase of the probability wave, $\theta$ will represent the mutual action of the two electrons.

This simple form applies only to Schrödinger's original theory in which there is but one $\psi$-function. In Dirac's theory there are four $\psi$-functions for one electron, and therefore 16 for two electrons. An extension of (2) is therefore required which will presumably introduce matrices. Since

$$e^{i\theta} = \cos\theta + i\sin\theta \,.\, 1,$$

the natural generalisation is to replace it by

$$\cos\theta + i\sin\theta \,.\, E_\mu,$$

where $E_\mu$ is one of the sixteen matrices (including 1) in my former paper. We *shall see, however, in § 5 that the corresponding matrices for the two-*electron problem are double and may conveniently be denoted by $E_\mu E_\nu'$. We therefore have in place of (2)

$$\Psi' = R(\theta, E_\mu E_\nu')\,\psi(q, q') = (\cos\theta + i\sin\theta \,.\, E_\mu E_\nu')\,\psi(q, q'). \qquad (3)$$

It is still true that increase of $\theta$ by $\pi$ reverses the sign of $\Psi'$, so that by the exclusion principle the conventional identity of the two electrons has been interchanged. Moreover the transformation which changes the identity now appears as part of the ordinary relativity investigation, because (except that they have been extended from one to two electrons) the transformations (3) are precisely those employed in my earlier paper (*loc. cit.* § 5) for investigating the relativity of space and time.

We might in fact have taken these rotations of the special relativity theory as our starting point. *When $\psi$ is "rotated" through an angle*, the space and time axes are rotated through the double angle. In the particular case when the double angle is $2\pi$ our space and time frame of reference has come back to its original position. What significance can we attribute to the fact that $\psi$ has as yet only performed half a revolution ? The answer is that that part of our frame of reference which does not relate to location in space and time but is concerned in assigning separate identity to indistinguishable electrons, may have gone through only a half-cycle and therefore be reversed. By thus associating a reversal of identity with the reversal of sign of $\psi$ by its half-revolution we reach the exclusion principle.

4. There will be a close parallelism between the angular "co-ordinate" $\theta$ that we have introduced and an angle $\phi$ specifying orientation in space. Both

are relative and have no determinate value until we have chosen an arbitrary reference origin for them. Both may be in various "planes," the planes of $\theta$ being distinguished by the various matrices $E_\mu E_\nu'$. Both are of the nature of ignorable co-ordinates; owing to their symmetry they do not enter directly into dynamical equations, but they may have angular momenta associated with them which are of dynamical importance. Further, such angular momenta will be quantised, since quantisation results from the necessity that $\psi$ should be a single-valued function of all angular variables. In the case of $\theta$ we already know from the exclusion principle that $\psi$ is singly periodic in $\theta$, so that the quantum number is fixed as unity.†

Let $r_{12}$ be the distance between the two electrons. More strictly it is the space-like interval between them and therefore an invariant; but in most applications the two electrons are considered at the same instant so that $r_{12}$ becomes the simple distance. If now $\theta$ is increased by $\pi$ there is a discordance between the spatial and the dynamical view of what has happened. The point P where the electron $e$ was has come back to P and the point P′ to P′, but the electron $e$ is now at P′ and the electron $e'$ at P. We are therefore justified in thinking of $\theta$ as an angle turned through by $r_{12}$. The turning, however, will be in directions outside our four-dimensional world, since a rotation $R\ (\theta, E_\mu)$ does not necessarily give purely internal transformations of space-time and a rotation for two electrons $R\ (\theta, E_\mu E_\nu')$ is a still more analytical conception; however the rotation if continued through an angle $\pi$ reverses $r_{12}$ end for end.

Hence $\partial/r_{12}\,\partial\theta$ is a symbolic momentum in the same way that $\partial/\partial x$ is a symbolic momentum. These symbols are interpreted by being placed between $\Psi^*$ and $\Psi$. viz. :—

$$\Psi^* \frac{\partial}{\partial x}\Psi, \qquad \Psi^* \frac{1}{r_{12}}\frac{\partial}{\partial\theta}\Psi.$$

But by (2) the second expression is equal to

$$\Psi^*\,(i/r_{12})\,\Psi,$$

so that $i/r_{12}$ is a symbolic momentum. For the corresponding matrix expression (3) we have

$$\begin{aligned}\frac{\partial\Psi}{\partial\theta} &= (-\sin\theta + i\cos\theta\,.\,E_\mu E_\nu')\,\psi\,(q, q') \\ &= iE_\mu E_\nu'\,(\cos\theta + i\sin\theta\,E_\mu E_\nu')\,\psi\,(q, q') = iE_\mu E_\nu'\Psi, \qquad (4)\end{aligned}$$

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† Higher quantum numbers would correspond to particles with integral multiples of the unit charge. It is conceivable that this might have some interest in connection with the charges of atomic nuclei.

since $(E_\mu E_\nu')^2 = 1$. Thus the symbolic momentum (comparable with $\partial/\partial x$) is

$$E_\mu E_\nu' \; (i/r_{12}). \tag{5}$$

From a geometrical standpoint it is unlikely that a rotation R would occur exactly in one of our chosen principal planes indicated by $E_\mu E_\nu'$, and we should have to resolve it into its components in these planes. But the conception of intermediate planes is difficult to deal with since the principal planes are not all perpendicular to one another (*loc. cit.* § 7). We shall here evade this by assuming that the idea of R being related to a particular plane is introduced only as a basis of statistics. When, therefore, in actual problems we suppose the direction of the plane to be at random, this condition will be considered to be more precisely expressed in the form that there is an equal $1/n$th chance of R being in each of the $n$ principal planes.

Accordingly the momentum (5) for a rotation R in the plane $E_\mu E_\nu'$ must be multiplied by the chance $1/n$ that R is in this plane, so that statistically the component momentum is

$$E_\mu E_\nu' \frac{i}{n r_{12}}. \tag{6}$$

It looks as though a difficult question might face us, viz., what to do with this θ-momentum when we have determined it; because it formally concerns the momentum of one electron relative to the other, whereas the wave-equation is concerned with sum of their momenta. The anticipated difficulty does not seem to arise, but I am not quite sure how (in a physical sense) it has settled itself. I think we have to regard its differential character in the following light. It represents transference of identity from one end of $r_{12}$ to the other; relative to our adopted reference system of identity this is a one-way process like an electric current (the opposite identity being transferred in the opposite direction), and this kind of *conduction* has to be combined additively with the *convection* described by dynamical motions. However that may be, we shall find on examining (6) that it is expressed as a stress. The difference between momentum and stress, which according to the relativity theory is somewhat artificial, practically disappears in wave-mechanics, and it is no great matter for surprise that the quantity canonically conjugate to θ turns out to be a stress. This, however, relieves any ambiguity as to how it is to be incorporated in the wave-equation since the other terms in the wave-equation also directly represent stresses.

5. In my earlier paper Dirac's four ψ-functions were distinguished by suffixes, It is now rather more convenient to regard the suffixes as the four permissible

values of a fifth co-ordinate $u$. For two electrons we shall have two such co-ordinates $u$, $u'$, giving 16 combinations. The matrices $E_\mu$ are then interchange-operators acting on $u$, and we must distinguish similar operators $E_\mu'$ acting on $u'$. The general interchange-operator is accordingly $E_\mu E_\nu'$. Its two factors are commutative, and either $E_\mu$ or $E_\nu'$ may in special cases be the matrix 1.

The wave-equation for a solitary electron is (*loc. cit.*, § 11)

$$H\psi = \left\{\frac{ih}{2\pi}\left(E_1\frac{\partial}{\partial x_1} + E_2\frac{\partial}{\partial x_2} + E_3\frac{\partial}{\partial x_3} + E_4\frac{\partial}{\partial x_4}\right) + mc\right\}\psi = 0, \tag{7}$$

where $E_1$, $E_2$, $E_3$, $E_4$ form a perpendicular set, and the fifth member $E_5$ might be used in place of 1 as the coefficient of $mc$ if desired. The separate equations for two electrons (of the same spin) may therefore be written

$$H\,\psi_a = 0, \qquad H'\psi_b' = 0.$$

(If they have opposite spin, the matrix $E_5$ or $E_5'$ must be used as coefficient of $mc$ in one but not in the other equation.) Multiplying by $\psi_b'$ and $\psi_a$ respectively, and adding, we find

$$(H + H')\,\psi_a\psi_b' = 0 \tag{8}$$

as the equation satisfied by the combined probability $\psi_a\psi_b'$.

When account is taken of their interaction the wave-equation for two electrons (of like spin) is understood to be*

$$\left\{H + H' + \frac{e^2}{cr_{12}}(E_1E_1' + E_2E_2' + E_3E_3' + E_4E_4')\right\}\Psi = 0. \tag{9}$$

The nature of this expression is more easily preceived if we divide through by $ih/2\pi$, and replace $2\pi e^2/hc$ by the number it stands for. Its numerical value is taken to be 1/136—the only likely number sufficiently near to the experimental value 1/137. The equation is then

$$\left\{\sum_{\mu=1}^{4}\left(E_\mu\frac{\partial}{\partial x_\mu} + E_\mu'\frac{\partial}{\partial x_\mu'} - \tfrac{1}{136}\,E_\mu E_\mu'\frac{i}{r_{12}}\right) - \frac{4\pi imc}{h}\right\}\Psi = 0. \tag{10}$$

This shows that in addition to the momenta $\partial/\partial x_\mu$ which appear when the electrons are treated separately, we have also to include certain components of the $\theta$-momentum calculated in (6). This seems to be a strong confirmation of our view that in introducing the factor $R(\theta, E_\mu E_\nu')$ in order to express the exclusion principle in a relativistic manner, we have introduced everything necessary to describe the mutual influence of two electrons. Comparing (6) and (10) it appears that we must have $n = 136$.

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* I obtain (9) by following out in my own notation a treatment given by J. A. Gaunt in a paper which will be published in these 'Proceedings.' I think that (9) is equivalent to his result. I use imaginary time ($x_4$) throughout this paper.

6. In counting the number of components $E_\mu E_\nu'$ it is necessary to regard $E_\mu E_\nu'$ as identical with $E_\mu' E_\nu$ and to avoid counting it twice over. To interchange the transformations applied to the domains of two electrons is meaningless since the electrons themselves have no separable identity. We might, however, have expected that a rotation $E_\mu E_\nu'$, which from our point of view includes two indistinguishable transformations, would have double weight as compared with $E_\mu E_\mu'$ which represents only one. The answer is given by the Einstein-Bose statistics. When two entities are indistinguishable their individuality disappears so completely that weights must be calculated without heed to it, and no extra weight is to be given to the cross-terms. In accordance with the Einstein-Bose principle we give equal weight to all the distinguishable rotations. Since there are 16 $E_\mu$'s and 16 $E_\mu'$'s, there will be 16 terms of form $E_\mu E_\mu'$ and 120 of form $E_\mu E_\nu'$, making 136 in all. Thus $n = 136$, as the equation (10) requires.

7. Whilst realising that the equations of wave-mechanics can only be interpreted statistically, we may be a little surprised that it should be permissible to use the statistical value of a momentum within the equation itself. But this is not out of keeping with other features of the wave-theory, in which averages replace fluctuating quantities in a way which seems very mysterious. This is especially illustrated in the theory of atomic radiation in which the change of electric moment, although it is professedly only a probable average, acts as a source of monochromatic light.

Some years ago one naturally expected that the value of $e$ would depend on the singular solution of some differential equation expressing the transition from charge to field. It was always difficult to see how such a theory could lead to the same charge in the very different conditions corresponding to an electron and proton. This kind of solution has been ruled out by the modern theory which has virtually abolished all structure of an electron. What we have in its place is a factor $2\pi e^2/hc$ which expresses a kind of property attributed to every pair of points in space ; it turns space from a mathematical conception into a possible site of physical phenomena by associating with a pair of points some degree of probability that they may be the scene of this interaction. There is no room for elaborate integrations or for differential equations in the theory of such a fundamental factor, and its numerical value ought to have a simple meaning. Again since $(i/r_{12})$ is at least formally a momentum, we can scarcely escape the conception of a momentum of which for some reason only 1/136th part comes into our space problems. We could not, I think, obtain so small a fraction without introducing 16 dimensions into our scheme so as to give room for a sufficient number of conceptual degrees of freedom. If this seems unduly elaborate for so elementary a phenomenon, we may point out that an equation involving a coefficient 1/136 cannot be quite the elementary thing it seems.

But actually the 16 dimensions have already appeared in our earlier paper as an essential container of Dirac's relativity scheme. Their most striking appearance is in § 15 (*loc. cit.*) where we find that the charge-current vector $j_\mu$ is an arbitrary selection of 4 out of 16 components of the obviously fundamental quantity $\psi^*\psi$. Thus even at that stage it was obvious that an attempt to elucidate the nature of electric charge and obtain its numerical value could not be restricted to the four components ordinarily recognised; and we are prepared to find that only a small component of the activity mathematically represented by $\psi^*\psi$ will appear in equations describing the internal properties of the four-dimensional world.

The 16 dimensions are merely conceptual, but the conception is a corollary to the introduction of matrices by Dirac. They need not describe reality, but they describe the mathematical scheme which is at present the accepted mode of solving some of the problems of reality.

8. Four particular components of 0-momentum appear in (10). Before we can say whether these were to be expected or not, we must examine the principles on which the wave-equation appears to have been built up. We make free use of classical analogies.

The so-called equation of motion of a quantity F is (for a Hamiltonian H)

$$\mathrm{HF} - \mathrm{FH} = \frac{ih}{2\pi}\dot{\mathrm{F}}. \tag{11}$$

In relativity theory the differentiation must be supposed to refer to a proper-time $ds$ conjugated to H. When H is the Hamiltonian for a single electron and F is an algebraic expression, (11) is equivalent to

$$\left(\mathrm{E}_1\frac{\partial}{\partial x_1} + \mathrm{E}_2\frac{\partial}{\partial x_2} + \mathrm{E}_3\frac{\partial}{\partial x_3} + \mathrm{E}_4\frac{\partial}{\partial x_4}\right)\mathrm{F} = \frac{d\mathrm{F}}{ds}. \tag{12}$$

We see that $\mathrm{E}_\mu = dx_\mu/ds$, as may be verified by substituting $\mathrm{F} = x_\mu$ in (12). Also since

$$j_\mu = \psi^*\mathrm{E}_\mu\psi = \psi^*\frac{dx_\mu}{ds}\psi \tag{13}$$

(first paper, equation (41)) we see that $dx_\mu/ds$ is the symbolic* expression for the charge and current. Again if $t_1$ is the coefficient of $E_1$, in H, we have (omitting constant factors)

$$\begin{aligned} \dot{t}_1 = Ht_1 - t_1H &= E_2(t_2t_1 - t_1t_2) + E_3(t_3t_1 - t_1t_3) + E_4(t_4t_1 - t_1t_4) \\ &= \sum_\mu E_\mu (\operatorname{curl} \kappa)_\mu, \end{aligned} \tag{14}$$

where $\kappa$ is the electromagnetic potential. Since $E_\mu$ is the symbolic charge and current, the right-hand side by ordinary electrodynamics gives the symbolic ponderomotive force of the extraneous electromagnetic field, which should be equal to the rate of increase of momentum of the system. Hence $t_1$ is the symbolic momentum.

The set of 16 quantities $E_\mu t_\nu$ is analogous to the stress-energy tensor of matter $T_{\mu\nu}$. For a single particle $T_{\mu\nu} = m\frac{dx_\mu}{ds}\frac{dx_\nu}{ds}$, so that if we regard the momentum $t_\nu$ as the equivalent of $m\,dx_\nu/ds$ and remember that $E_\mu = dx_\mu/ds$, the correspondence is evident. Also the action $T = g^{\mu\nu}T_{\mu\nu}$. Hence the wave analogue of action is $g^{\mu\nu}E_\mu t_\nu$, which for Euclidean values of the $g$'s becomes

$$g^{\mu\nu}E_\mu t_\nu = E_1t_1 + E_2t_2 + E_3t_3 + E_4t_4. \tag{15}$$

This is the combination found in the wave-equation.

We have to examine what place the 0-momenta should have in this combination. They may be written

$$\frac{1}{136}\frac{i}{r}\frac{dx_\mu}{ds}\frac{dx_\nu'}{ds}. \tag{16}$$

Since $r$ is an invariant it will be seen that they are already in the form of a stress-energy tensor (*i.e.*, contain two velocity-factors) and are therefore ready for inclusion in T unmodified. If we multiply them by $g^{\mu\nu}$, as we did the $E_\mu t_\nu$, we obtain precisely the additional terms in (10). The question of the sign to be attributed to them is not settled by our theory because of the ambiguity of the two roots of $-1$. The $i$ factor in these terms has no connection with the $i$ in the last term of (10), and it need not denote the same root. This ambiguity is useful because the theory of the charge of a proton must evidently follow practically the same lines (though we are not yet prepared to formulate it definitely†) and it would be a serious objection if the theory forbade attractive forces.

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[*] The description "symbolic" is applied to a quantity interpreted by being placed between $\psi^*$ and $\psi$.

It will be noticed that we are nowhere concerned with the masses of the electrons.

At first sight it seems illegitimate to employ the Euclidean $g^{\mu\nu}$ for axes $x_\mu$, $x_\nu'$ which do not belong to the same space. I think the answer is that the wave-equation describes the connection between the probability distribution $\Psi$ of electron pairs in space and its gradients $\partial\Psi/\partial x_\mu$ ; before we can connect this with the corresponding problem for separate electrons we must remove effects arising from confusion of identity of the two electrons. To discover these effects we have pursued out investigations in as many degrees of freedom as the system admits ; but in removing them the question is, not what is their proper origin, but how they will have been represented in the space we are discussing. We have (mistakenly, if you like) represented $x$ and $x'$ as the same direction in a single space ; we must also regard them in this way in removing the effects of the mistake.

9. The following is, as well as I can judge, the general conclusion that is reached. Suppose that we are given the positions of a number of particles at two consecutive instants. If we are also given the connection of identity of the particles at the two instants we can determine their motions and hence find the various components of stress. But if the identity is unknown or non-existent the problem of finding the stresses is indeterminate ; it makes all the difference how we connect the particles in the two configurations each to each. The observed change of distribution can therefore only be treated as a combination of two parts (1) an actual flow of particles which makes a genuine contribution to the stresses, (2) a " flow of identity " which makes a spurious contribution to the calculated stresses. Now for one electron the wave-equation gives a connection between the distribution and the stresses. If we are to have a corresponding equation for more than one electron it will be essential to discriminate between the genuine and the spurious stresses, and to insert terms in the equation removing the part of the stresses calculated from the ordinary formula $(E_\mu t_\nu)$ which merely represents flow of identity.

The problem is only determinate because the flow of identity is *quantised* ; that is to say, it is connected with an angular variable which must necessarily be single-valued. Relativity theory alone would tell us that if electrons have no absolute individuality, the $\psi$-functions for one assignment of identity of two electrons must be some linear transformation of the $\psi$-functions corresponding to the reversed assignment. The exclusion principle tells us that the transformation in question is a multiplication by $-1$. We turn to the relativity theory (developed in the previous paper) to show what are the continuous transformations which lead to this, and we see that most of them lie outside our four-dimensional world. Our object is to remove that part of the flow that could and would be mistaken for a flow of particles from point to point in space-time. Of the 136 components we easily pick out one which must correspond to some kind of stress in the $x$ direction since it is covariant with $dx\,dx'$, and therefore with $dx^2$, in our four-dimensional world. This is evidently the spurious stress that has to be removed from $E_1t_1$; it has made it appear that particles have been rushing to and fro changing places, whereas all that has been interchanged is their labels. By the same argument three other spurious stresses are removed; and we reach equation (10) without any ambiguity, except that the two $i$'s in the equation are not proved to be the same root of $-1$.

# *On the Theory of the Solar Diurnal Variation of the Earth's Magnetism.*

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## *Introduction.*

1. The most likely explanation of the solar diurnal magnetic variation (conveniently denoted by S) has for more than a generation seemed to be that afforded by the "dynamo" theory, originally proposed by Balfour Stewart and further developed by Schuster and the writer.* It attributes S to overhead electric currents, induced by convective motion of the air across the earth's magnetic field. The form and intensity of the current-system can be inferred from the spherical harmonic analysis of S; J. Bartels,† on the basis of the writer's analysis, has drawn the current-diagram reproduced in the figure (p. 383). It will be seen that the current-system consists of four circuits, two north and two south of the equator, each flowing round a centre or focus. At the equinoxes, to which the figure refers, the system is approximately symmetrical with respect to the equator. The principal pair of circuits are situated in the sunlit hemisphere, and each circuit of this pair carried 62,000 amperes at sunspot minimum; their foci lie approximately on the 11 hour meridian. The other pair of circuits, each carrying 32,000 amperes, are less intense but more

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* For references *cf.* 'Phil. Trans.,' A, vol. 218, p. 1 (1919).

† J. Bartels, "Handbuch exp. Physik," vol. 25 (1928).

extensive, covering about 15 hours in longitude. The equatorial current-intensity, per centimetre measured along the meridian, has an eastward maximum of $2 . 10^{-5}$ e.m.u. at about 11h, and a westward maximum of $10^{-5}$ e.m.u. at about 17h.

2. The dynamo theory can give a good account of the general form of this current-system, but meets serious difficulties when it attempts to explain the phase and intensity of the currents. This is because the convective motion which induces the currents, and the total conductivity of the layer in which they flow, are unknown. But if it is assumed that the convective motion is the same as at ground level, it appears that the day current-foci should be on the meridian 13h or 14h, distinctly later than the observed position. Further, the total electric conductivity (or $\int \sigma \, dh$, the integral of the specific conductivity $\sigma$ throughout the thickness of the layer) must be large, of the order $10^{-5}$ e.m.u.

3. Until recently no independent check on this estimate of $\int \sigma \, dh$ was available, but radio data now give information concerning the electron-density at great heights, and confirm the existence of a highly conducting layer. But it is still doubtful whether the total conductivity of the layer is so great as $10^{-5}$; P. O. Pedersen, in his recent valuable and comprehensive discussion of radio propagation,* concludes (*loc. cit.*, p. 149) that it is only $5 . 10^{-7}$, or about 20 times too small.

4. The free charges in the upper air seem likely to consist mainly of electrons and singly ionised nitrogen or oxygen molecules. It is convenient to treat the latter as of equal mass, corresponding to a molecular weight of about 30. Symbols for quantities relating to electrons, positive or negative ions, or ions without distribution of sign, will be distinguished by the suffixes $e$, $+$, $-$, $i$. Let $m$ be the mass of a free charge, $n$ the number per cubic centimetre, $\nu$ the number of collisions which it undergoes per second, $e$ its charge in electromagnetic units. Then we take

$$m_e = 9 \cdot 0 . 10^{-28}, \quad m_i = 5 \cdot 0 . 10^{-23}, \quad e = \pm 1 \cdot 59 . 10^{-20}.$$

The specific conductivity $\sigma$ of the gas is due to contributions $\sigma_e$ or $\sigma_i$ of each individual electron or ion, *i.e.*,

$$\sigma = n_e \sigma_e + n_i \sigma_i. \tag{1}$$

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* P. O. Pedersen, "The Propagation of Radio Waves," Copenhagen, 1927.

In the absence of a magnetic field, approximately

(2) $$\sigma_e = e^2/m_e\nu_e, \quad \sigma_i = e^2/m_i\nu_i,$$

so that the rarer the gas, and the less frequent the collisions, the greater are $\sigma_e$ and $\sigma_i$.

5. Pedersen made an important contribution to the theory of the conductivity by recognising that in a magnetic field the conductivity is different in different directions, its value for directions along the field being the same as if the field were absent, but its value (conveniently denoted by $\sigma_\perp$) for directions transverse to the field being reduced in the ratio

(3) $$K = \nu^2/(\nu^2 + \omega^2),$$

where

(4) $$\omega = eH/m,$$

$\omega$ being the angular velocity with which the charge spirals freely round the lines of magnetic force. Since $\nu$ and $\omega$ are different for ions and electrons, the corresponding ratios $\sigma_\perp/\sigma$ or K are likewise different; we have

(5) $$\sigma_\perp = n_e\sigma_{e\perp} + n_i\sigma_{i\perp} = n_e K_e\sigma_e + n_i K_i\sigma_i = \frac{n_e e^2}{m_e}\frac{\nu_e}{\nu_e^2 + \omega_e^2} + \frac{n_i e^2}{m_i}\frac{\nu_i}{\nu_i^2 + \omega_i^2}$$

so that as $\nu$ tends to zero $\sigma_\perp$ tends also to zero* instead of to infinity like $\sigma$.

This result is of importance to the theory of S because the currents illustrated in the figure flow transversely to the magnetic meridians over a considerable fraction of their path, and even when the flow is in the magnetic meridian planes it is partly transverse to the magnetic field, since the current-flow is nearly horizontal, while except in low latitudes the magnetic force has a considerable vertical component. Hence the total resistance round any current-line is determined mainly by $\sigma_\perp$, especially when $\sigma_\perp/\sigma$ is small. The conducting layer is therefore effectively limited by the value of $\sigma_\perp$, and this places a hitherto unsuspected limit on the upward extension of the layer: it will appear later that the layer must probably lie approximately between 100 and 170 km. height above the ground (§ 9).

6. Regarding the earth's magnetic field as that of a sphere uniformly magnetised along the axis of rotation,

(6) $$\omega = eH/m = (eH_0/m)(1 + 3\cos^2\theta)^{\frac{1}{2}},$$

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* Ross Gunn, 'Phys. Rev.,' vol. 32, p. 133 (1928), has also remarked the same result, apparently without knowledge of Pedersen's work.

where $H_0$ denotes the equatorial magnetic intensity, and $\theta$ denotes the north-polar-distance in angle. Approximately

$$H_0 = 0 \cdot 3 \text{ gauss.} \tag{7}$$

Inserting the values of $e$, $H_0$ and $m$,

$$\omega_e = 5 \cdot 3 \,.\, 10^6 \,(1 + 3 \cos^2 \theta)^{\frac{1}{2}}, \quad \omega_i = 95 \,(1 + 3 \cos^2 \theta)^{\frac{1}{2}}. \tag{8}$$

7. The value of $\nu$ varies with the height $h$ in a way which depends on the distribution of absolute temperature T and on the composition of the air; these are not definitely known at great heights. But it is probably not far from the truth to take T = 220° in the stratosphere up to 60 km., and 300° above 80 km., with a uniform transition between these heights; and, further, to assume that convection keeps the composition uniform up to 110 km.; and thereafter ceases. In this case the air will consist almost wholly of $N_2$ and $O_2$ up to 200 km., since even if helium be present at 110 km. in the proportion observed near the ground, it will only amount to 2 per cent. at 200 km.; the proportion of oxygen will be 21 per cent. at 110 km., 13 per cent. at 150 km. and 6 per cent. at 200 km., nitrogen being the only other important constituent.

The electrons and ions will be assumed to have speeds $v$ corresponding to thermal equilibrium*; hence above 80 km., where T = 300°,

$$v_e = 1 \cdot 1 \,.\, 10^7 \text{ cm./sec.}, \quad v_i = 4 \cdot 7 \,.\, 10^4 \text{ cm./sec.} \tag{9}$$

The mean free path $l$ will be supposed related to the pressure $p$ (in dynes/cm.$^2$) by the equations

$$l_e = 43/p, \quad l_i = 6/p. \tag{10}$$

The above assumptions concerning the atmosphere enable $p$ to be calculated at any height, and hence, using (9), (10) and

$$\nu = v/l, \tag{11}$$

the values of $\nu$ given in Table I have been determined; the table also gives values of $K_e$ and $K_i$, and of $1 - K_e$, $1 - K_i$, calculated from the values of $\nu$ and of $\omega$ (*cf.* 8), for the equator and the polar regions.

The above values of $\nu$, and hence of K, differ from those given by Pedersen, because he assumed that T = 220° at all heights in the stratosphere, and that mixing by convection ceases at 12 km. The first assumption is contrary to three independent lines of evidence, which support a higher temperature

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* Townsend and Tizard, 'Roy. Soc. Proc.,' A, vol. 88, p. 347 (1913).

Table I.

| Height. | 60. | 70. | 80. | 90. | 100. | 110. | 120. | 130. | 140. | 150. |
|---|---|---|---|---|---|---|---|---|---|---|
| $\nu_e$ | $3{\cdot}3 \,.\, 10^7$ | $10^7$ | $3{\cdot}3 \,.\, 10^6$ | $1{\cdot}1 \,.\, 10^6$ | $3{\cdot}5 \,.\, 10^5$ | $1{\cdot}2 \,.\, 10^5$ | $3{\cdot}8 \,.\, 10^4$ | $1{\cdot}3 \,.\, 10^4$ | $4{\cdot}4 \,.\, 10^3$ | $1{\cdot}5 \,.\, 10^3$ |
| $\nu_i$ | $10^6$ | $3 \,.\, 10^5$ | $10^5$ | $3{\cdot}5 \,.\, 10^4$ | $1{\cdot}1 \,.\, 10^4$ | $3{\cdot}6 \,.\, 10^3$ | $1{\cdot}2 \,.\, 10^3$ | $4 \,.\, 10^2$ | $1{\cdot}3 \,.\, 10^2$ | $4{\cdot}7 \,.\, 10$ |
| $(K_e)$ eq. | 0·975 | 0·74 | 0·28 | $4 \,.\, 10^{-2}$ | $4 \,.\, 10^{-3}$ | $5 \,.\, 10^{-4}$ | $5 \,.\, 10^{-5}$ | $6 \,.\, 10^{-6}$ | $7 \,.\, 10^{-7}$ | $8 \,.\, 10^{-8}$ |
| $1 - (K_e)$ eq. | 0·025 | 0·26 | 0·72 | 0·96 | 1·00 | 1·00 | 1·00 | 1·00 | 1·00 | 1·00 |
| $(K_e)$ pole | 0·907 | 0·41 | 0·08 | $1{\cdot}1 \,.\, 10^{-2}$ | $1{\cdot}1 \,.\, 10^{-3}$ | $1{\cdot}3 \,.\, 10^{-4}$ | $1{\cdot}3 \,.\, 10^{-5}$ | $1{\cdot}5 \,.\, 10^{-6}$ | $1{\cdot}7 \,.\, 10^{-7}$ | $2 \,.\, 10^{-8}$ |
| $1 - (K_e)$ pole | 0·093 | 0·59 | 0·92 | 0·99 | 1·00 | 1·00 | 1·00 | 1·00 | 1·00 | 1·00 |
| $(K_i)$ eq. | 1·00 | 1·00 | 1·00 | 1·00 | 1·00 | 1·00 | 0·99 | 0·94 | 0·65 | 0·20 |
| $1 - (K_i)$ eq. | $10^{-8}$ | $10^{-7}$ | $10^{-6}$ | $8 \,.\, 10^{-6}$ | $8 \,.\, 10^{-5}$ | $8 \,.\, 10^{-4}$ | $6 \,.\, 10^{-3}$ | $6 \,.\, 10^{-2}$ | 0·35 | 0·80 |
| $(K_i)$ pole | 1·00 | 1·00 | 1·00 | 1·00 | 1·00 | 1·00 | 0·98 | 0·81 | 0·32 | 0·06 |
| $1 - (K_i)$ pole | $4 \,.\, 10^{-8}$ | $4 \,.\, 10^{-7}$ | $4 \,.\, 10^{-6}$ | $3 \,.\, 10^{-5}$ | $3 \,.\, 10^{-4}$ | $3 \,.\, 10^{-3}$ | $2{\cdot}5 \,.\, 10^{-2}$ | 0·19 | 0·68 | 0·94 |

above about 60 km., as here supposed; they are (i) the observations of meteor trails as interpreted by the theory of Lindemann and Dobson,* (ii) the observations of abnormal sound-propagation to great distances,† (iii) the theoretical calculation of upper air temperatures, taking into account the known layer of ozone in the stratosphere.‡ The second assumption is contrary to the evidence of mixing afforded by the contortions usually observed in long-enduring meteor-trails, and notably in the one, lasting for nearly 2 hours, observed by Mr. J. E. Clarke§ and others, on February 22, 1909. This trail, 150 miles long, sloping slightly downwards from a height of 90 km. above a point 45 miles 26° W. of S. from Beachy Head to a height of 77 km. above a point, 87 miles 22° E. of S. from Start Point, became distorted in such a way as to indicate high level winds showing the following remarkable differences of intensity and direction at heights of 50 to 55 miles (80 to 90 km.).

| Approximate height. | | Speed. miles/hour. | Mean direction. |
|---|---|---|---|
| Miles. | Km. | | |
| 55 | 88·5 | 111 | NE by E |
| 54 | | 135 | NE by N |
| 53 | | 135 | NW |
| 52 | | 175 | WNW |
| 51·5 | | 187 | W by N |
| 50 | 80·5 | 30 | S |
| 50 | | 170 | E |

Such long-enduring trails are rare, but less exceptional instances are available which give similar evidence of intense non-uniform winds, of the order of 100 miles per hour, at heights extending up to 130 km. These winds are probably due to large temperature variations set up in the atmosphere, not only as between day and night, but also from day to day and from place to place. Large temperature variations will arise from variations (such as are actually observed) in the amount of ozone, which has so great an influence on the temperature of the upper stratosphere; and also from the considerable variations, up to 100 per cent., in the sun's ultra-violet radiation, as observed by Pettit.‖

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* 'Roy. Soc. Proc.,' A, vol. 102, p. 411 (1922).

† F. J. W. Whipple, 'Nature,' vol. 111, p. 187 (1923).

‡ Gowan, 'Roy. Soc. Proc.,' A, vol. 120, p. 655 (1928).

§ 'Q. J. R. Met. Soc.,' vol. 39, p. 115 (1913).

‖ 'Proc. Nat. Acad. Sci.,' vol. 130, p. 380 (1927).

Such strong and non-uniform winds must promote mixing of the air up to heights exceeding 100 km., and it seems likely that they are capable of effectively counteracting the tendency towards diffusive separation of the atmospheric constituents according to their molecular weights; this process is extremely slow, at least up to 100 km. It is here assumed that the mixing ceases at 110 km. Pedersen's assumption that it ceases at 12 km. results in a rapid increase in the proportion of helium above 90 km., until at 130 km. it is 90 per cent. of the whole air. This is rendered improbable by the fact that no spectral lines that can be attributed to helium are observed in auroræ, although the excitation would seem sufficient to produce such lines were helium present.

The low temperature assumed by Pedersen renders the upward decrease of pressure too rapid until heights are reached where helium is an important constituent, and thereafter the decrease of pressure is too slow. Hence his values of $\nu$ at 100 km. are only one-third those given in Table I, while at 150 km. they are 10 times as great. The effect of these differences on the values of K is easily inferred.

8. The number of electrons and ions at great heights is uncertain. Pedersen gives the following values (*loc. cit.*, Appendix, p. 10, fig. IX, 6), based partly on radio measurements and partly on a theory of ionisation and recombination; they refer to noon in summer, at some latitude apparently not stated, which will here be assumed to be that of the equator.

Table II.

| Height. | 60. | 70. | 80. | 90. | 100. | 110. | 120. | 130. | 140. | 150. | 160. | 170. | 180. | 190. | 200. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $n_e$ | $<1$ | $<1$ | $<1$ | 1 | $3 . 10^3$ | $1{\cdot}6 . 10^4$ | $5 . 10^5$ | $7 . 10^5$ | $5 . 10^5$ | $4 . 10^5$ | $2 . 10^5$ | $1{\cdot}3 . 10^5$ | $5 . 10^4$ | $3 . 10^4$ | $1{\cdot}2 . 10^4$ |
| $n_i$ | $7 . 10^3$ | $6 . 10^3$ | $3 . 10^3$ | $5 . 10^4$ | $2 . 10^6$ | $10^7$ | $8 . 10^6$ | $4 . 10^6$ | $2 . 10^6$ | $7 . 10^5$ | $3 . 10^5$ | $1{\cdot}3 . 10^5$ | $5 . 10^4$ | $3 . 10^4$ | $1{\cdot}2 . 10^4$ |

According to this table the electron density first becomes important at about 100 km.; below this the electrons are supposed to attach themselves to oxygen or water molecules as soon as they are formed. Above 170 km. the amount of such recombination is supposed negligible, owing to the low density, and $n_e = n_i = n_+$, $n_- = 0$. At all heights the air is practically neutral, *i.e.*,

$$(12) \qquad n_+ = n_- + n_e, \quad n_i = n_+ + n_- = 2n_+ - n_e.$$

If each of the above values of $n_e$ and $n_i$ is taken to apply throughout a 10 km. layer ($10^6$ cm.) the total numbers ($N_e$, $N_i$) of each, per square centimetre column, are approximately

$$(13) \qquad N_e = 2\cdot6 \, . \, 10^{12} \quad , \quad N_i = 2\cdot8 \, . \, 10^{13}.$$

9. On substituting the above values of $n_e$, $n_i$, $K_e$, $K_i$ into (2)–(4), we obtain the following values of $n_e\sigma_e$, $n_i\sigma_i$ and $\sigma$, both along and transverse to the magnetic field at the equator. The contributions of the layers below 100 km. are negligible in comparison with those of the higher strata, and are therefore not indicated.

Table III.

| Height. | 100. | 110. | 120. | 130. | 140. | 150. |
|---|---|---|---|---|---|---|
| $n_e\sigma_e$ | $2\cdot4 \, . \, 10^{-15}$ | $3\cdot7 \, . \, 10^{-14}$ | $3\cdot7 \, . \, 10^{12}$ | $1\cdot5 \, . \, 10^{-11}$ | $3\cdot2 \, . \, 10^{-11}$ | $8 \, . \, 10^{-11}$ |
| $n_i\sigma_i$ | $10^{-15}$ | $1\cdot6 \, . \, 10^{-14}$ | $3\cdot8 \, . \, 10^{-14}$ | $5\cdot6 \, . \, 10^{-14}$ | $9 \, . \, 10^{-14}$ | $8 \, . \, 10^{-14}$ |
| $\sigma$ | $3 \, . \, 10^{-15}$ | $5 \, . \, 10^{-14}$ | $3\cdot7 \, . \, 10^{-12}$ | $1\cdot5 \, . \, 10^{-11}$ | $3\cdot2 \, . \, 10^{-11}$ | $8 \, . \, 10^{-11}$ |
| $n_e\sigma_{e\perp}$ | $10^{-17}$ | $2 \, . \, 10^{-17}$ | $2 \, . \, 10^{-16}$ | $9 \, . \, 10^{-17}$ | $2 \, . \, 10^{-17}$ | $6 \, . \, 10^{-18}$ |
| $n_i\sigma_{i\perp}$ | $10^{-15}$ | $1\cdot6 \, . \, 10^{-14}$ | $3\cdot8 \, . \, 10^{-14}$ | $5\cdot3 \, . \, 10^{-14}$ | $5\cdot9 \, . \, 10^{-14}$ | $1\cdot6 \, . \, 10^{-14}$ |
| $\sigma_\perp$ | $10^{-15}$ | $1\cdot6 \, . \, 10^{-14}$ | $3\cdot8 \, . \, 10^{-14}$ | $5\cdot3 \, . \, 10^{-14}$ | $5\cdot9 \, . \, 10^{-14}$ | $1\cdot6 \, . \, 10^{-14}$ |

According to this table the conductivity along the magnetic field is almost wholly due to the electrons, and increases upwards to at least 150 km. The transverse conductivity, on the other hand, is almost wholly due to the ions, and attains its maximum value at about 135 km., and does not extend much above 150 km.

The estimate of $\int \sigma_\perp \, dh$ afforded by the table is found to be $2 \, . \, 10^{-6}$ e.m.u. Pedersen's estimate is $0\cdot5 \, . \, 10^{-6}$ e.m.u. or one-quarter the value here found, the difference resulting from his different assumptions concerning the temperature and composition of the stratosphere.

The value of $\int \sigma_\perp \, dh$ here found is of the same order as that ($10^{-5}$) required by the dynamo theory, though rather smaller, *i.e.*, in the ratio one-fifth. The difference is probably within the present limits of error of the data for $n_e$ and $n_i$; more accurate knowledge later may either narrow or widen the gap between the two estimates of the conductivity. The estimated conductivity required by the dynamo theory is capable of modification by supposing that the convective motion in the conducting layer is different from that observed near the ground.

9. R. Gunn* has recently pointed out that in the layers where $\nu/\omega$ is small, that is, where a free charge can execute many revolutions in its spiral paths between successive collisions, the spiral motion makes the charge equivalent to a small magnet opposed to the field, so that the ionised medium is diamagnetic. The contribution of each free charge to the intensity of magnetisation of the medium is the same for electrons and ions when $\nu/\omega$ is very small, being $k\mathrm{T}/\mathrm{H}$, where $k$ is Boltzmann's constant $(1 \cdot 37 \,.\, 10^{-16})$; when $\nu/\omega$ is not small, it is easily shown that the contribution is reduced in the ratio

$$\omega^2/(\nu^2 + \omega^2) = 1 - \mathrm{K} ;$$

thus the fractional contributions of a free charge to the transverse conductivity $\sigma_\perp$ and to the diamagnetisation are complementary. Table I shows that the electrons contribute almost their full quota to the diamagnetism from 90 km. upwards, so that the conducting layer is rendered diamagnetic by the electrons; the ions only begin to contribute fully to the diamagnetism at about 150 km., near where the conducting layer ceases (according to the values of $n_e$ and $n_i$ in Table II).

Gunn has suggested that this diamagnetic layer of the upper atmosphere, of intensity

$$(14) \qquad (k\mathrm{T}/\mathrm{H}) \int \{(1 - \mathrm{K}_e)\, n_e + (1 - \mathrm{K}_i)\, n_i\}\, dh = (k\mathrm{T}/\mathrm{H})\mathrm{N}_d,$$

is responsible for the diurnal magnetic variations, owing to the daily variation of the magnetic field of the layer, as $n_e$ and $n_i$ vary. He has partly worked out the resulting magnetic variations, assuming a probable variation of $\mathrm{N}_d$ with the sun's zenith distance, and has shown that they are in fairly good qualitative agreement with the observed S. In another paper I have developed the theory further, by means of spherical harmonic analysis, and have confirmed his general conclusion. In order to bring the theory into approximate agreement with observation, only one unknown magnitude has to be assumed, namely, the number $\mathrm{N}_d$ defined by the above equation; $\mathrm{N}_d$ may be called the number of diamagnetically effective free charges per square centimetre column. According to Gunn, its maximum value, occurring at the equator at noon, must be $1 \cdot 5 \,.\, 10^{17}$; my own estimate, which seems likely to be more accurate, is $5 \,.\, 10^{16}$.

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[*] 'Phys. Rev.,' vol. 32, p. 133 (1928).

This value, which includes practically all the electrons and a fraction of the ions, namely, those above about 145 km., is far larger than that to be deduced from Pedersen's discussion, according to which $N_e$ is about $2{\cdot}6 \,.\, 10^{12}$, and $(N_i)_d$, or $\int (1 - K_i)\, n_i \, dh$, is about $10^{12}$, so that $N_d$ is less than $4 \,.\, 10^{12}$. The discrepancy between the ionisation as estimated by Pedersen, and that required by the diamagnetic theory of S, is far more extreme than in the case of the dynamo theory, the ratio (required N/estimated N) being $10^4$ instead of about 10.

10. Pedersen's estimates of $n_e$ and $n_i$ seem likely to be more accurate for heights up to about 150 km. (that is, within the conducting layer) than at greater heights. Since his discussion was written, E. V. Appleton has found that in the early morning during the three hours before sunrise, when the ionisation in the conducting layer has become much reduced by recombination, 400 metre waves that are usually reflected in this layer penetrate it and pass upwards till they meet another reflecting ionised layer at about 250 km. height. This suggests that $n_e$ and $n_i$ at heights above 150 km. may be much greater than Pedersen supposes, though the change in his figures would need to be revolutionary if S is to be attributed to the diamagnetism of the upper atmosphere. It will be shown, however, that the ions in the diamagnetic region can contribute to S far more effectively in another way, and that $N_d$ must be of the order $2 \,.\, 10^{14}$ at most.

11. Consider the motion of a free charge in the presence of a uniform magnetic field of intensity H. Let the axis of $z$ be taken along H. Suppose that a constant force F acts upon the charge, and take the $x$ axis in the plane of F and H, and so that the $x$-component (X) of F is positive; let the third axis $0y$ be chosen so that the axes form a right-handed system. Then $F = (X, 0, Z)$.

The equations of motion of the particle are

$$m\ddot{x} = X + eH\dot{y}, \tag{15}$$

$$m\ddot{y} = -\, eH\dot{x}, \tag{16}$$

$$m\ddot{z} = Z, \tag{17}$$

of which the integrals are

$$\dot{x} = \dot{x}_0 \cos \omega t + \dot{y}_0 \sin \omega t - (X/eH) \sin \omega t, \tag{18}$$

$$\dot{y} = -\, \dot{x}_0 \sin \omega t + \dot{y}_0 \cos \omega t - (X/eH)\,(1 - \cos \omega t), \tag{19}$$

$$\dot{z} = \dot{z}_0 + (Z/m)t, \tag{20}$$

where the suffix 0 refers to the initial values.

The motion along the field is unaffected by H, but the mean value of $\dot{x}$ is zero, despite the force X; this is why $\sigma_\perp$ tends to zero with $\nu/\omega$. But the force X renders the mean transverse velocity $\dot{y}$, which would otherwise be zero, equal to

$$-(X/eH). \tag{21}$$

This mean transverse velocity will be called the drift-velocity V of the free charge.

12. If the free charge forms part of a gas, and makes $\nu$ collisions per second with other particles, after which its velocity takes a new direction at random, it is easy to show that the mean $y$-velocity is

$$(1-K)(X/eH), \tag{22}$$

where K is defined by (3). Thus the less the contribution ($K\sigma$) made by the charge to $\sigma_\perp$, the greater the mean drift-velocity which it experiences, and *vice versa.*

13. The drift-motions of the charges give rise to a current of intensity $i$, where

$$i = (1/H)\{(1-K_i)(n_+X_+ + n_-X_-) + (1-K_e)\,n_eX_e\}, \tag{23}$$

assuming that the positive and negative ions are of equal mass.

14. In the ionised atmosphere the light electrons tend to rise above the heavier ions, but this sets up an electrostatic field which prevents all but a very slight separation, so that the medium remains practically neutral, in accordance with (12). The field is smaller, the greater the proportion of negative ions to electrons, because the field due to the rise of the electrons tends to depress the negative ions, and therefore to produce a compensating opposing field.

When the conditions are steady, the equations of partial pressure for the three kinds of free charge are as follows,

$$\frac{\partial p_+}{\partial h} = -n_+(m_+g - Ee), \tag{24}$$

$$\frac{\partial p_-}{\partial h} = -n_-(m_-g + Ee), \tag{25}$$

$$\frac{\partial p_e}{\partial h} = -n_e(m_eg + Ee), \tag{26}$$

where $p = knT$, $k$ being Boltzmann's constant $1\cdot37\,.\,10^{-16}$, and E denotes the electric field, reckoned positive when upwards. We may write $m_+ = m_- = m_i$, and ignore $m_e$, in (24) to (26). By (12)

$$(27) \qquad \frac{\partial p_+}{\partial h} = \frac{\partial(p_- + p_e)}{\partial h},$$

so that

$$(28) \qquad n_+ (m_i g - \mathrm{E}e) = n_- (m_i g + \mathrm{E}e) + n_e \mathrm{E}e = n_- m_i g + n_+ \mathrm{E}e,$$

or

$$(29) \qquad \mathrm{E}e = \tfrac{1}{2} (n_e/n_+)\, m_i g.$$

The vertically downward forces F on the free charges are therefore given by

$$(30) \qquad \mathrm{F}_e = \frac{n_e}{n_i + n_e} m_i g, \quad \mathrm{E}_+ = \frac{n_i}{n_i + n_e} m_i g, \quad \mathrm{F}_- = \frac{n_i + 2n_e}{n_i + n_e} m_i g.$$

15. Regarding the earth's magnetic field as that of a sphere uniformly magnetised along the axis of rotation, the downward vertical and northward horizontal components of H at north-polar-distance $\theta$ are

$$(31) \qquad 2\mathrm{H}_0 \cos\theta, \quad \mathrm{H}_0 \sin\theta,$$

so that

$$(32) \qquad \mathrm{H}^2 = \mathrm{H}_0^2 (1 + 3\cos^2\theta).$$

The $z$ axis, as defined in § 11, is therefore northward and downward, while the $x$ axis is southward and downward, and the $y$ axis is horizontal and westward. The $x$ components of the forces F on the free charges are equal to

$$(33) \qquad \mathrm{F} \sin\theta/(1 + 3\cos^2\theta)^{\frac{1}{2}}.$$

Hence, by (23, 30, 33), the drift-current intensity is given by

$$(34) \qquad i = -\frac{m_i g \sin\theta}{\mathrm{H}_0 (1 + 3\cos^2\theta)} \left\{ (1 - \mathrm{K}_i) \frac{n_i^2 + n_i n_e - n_e^2}{n_i + n_e} + (1 - \mathrm{K}_e) \frac{n_e^2}{n_i + n_e} \right\}$$
$$\equiv -\frac{m_i g \sin\theta}{\mathrm{H}_0 (1 + 3\cos^2\theta)} n'.$$

Since $i$ is essentially negative, the drift-current is everywhere eastward.

16. The drift-velocity V of a free charge is greatest at the equator, where $\mathrm{X} = \mathrm{F}$ and H has its minimum value. At heights where $\mathrm{K} = 1$, and $n_e = n_i$, $\mathrm{V}_e = \mathrm{V}_i = \frac{1}{2} m_i g/e\mathrm{H}$, which at the equator is 5·1 cm./sec. If $\mathrm{K} = 1$ but $n_e < n_i$, $\mathrm{V}_e$ lies between 0 and 5·1, while $\mathrm{V}_+$ lies between 5·1 and 10·2, and $\mathrm{V}_-$ lies between 10·2 and 15·3 cm./sec. For given values of K, $n_e$, $n_i$, these velocities decrease from the equator to the pole in proportion to the factor $\sin\theta/(1 + 3\cos^2\theta)$, the value of which is given for various latitudes in the following table.

Table IV.

| Latitude | 0° | 10° | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° |
|---|---|---|---|---|---|---|---|---|---|---|
| $\theta$ | 90° | 80° | 70° | 60° | 50° | 40° | 30° | 20° | 10° | 0° |
| $\sin\theta/(1+3\cos^2\theta)$ | 1 | 0·904 | 0·696 | 0·495 | 0·342 | 0·233 | 0·153 | 0·094 | 0·044 | 0 |

17. The equatorial values of $(1-K_e)$ and $(1-K_i)$ are practically unity from 160 km. upwards, so that from Table I, II the following table giving the value of $n'$, corresponding to Pedersen's data for $n_e$ and $n_i$, can be constructed.

Table V.

| Height (km.) | 100 | 110 | 120 | 130 | 140 | 150 |
|---|---|---|---|---|---|---|
| $(1-K_e)\dfrac{n_e^2}{n_i+n_e}$ | 4 | 26 | $3 . 10^4$ | $10^5$ | $10^5$ | $1·5 . 10^5$ |
| $(1-K_i)\dfrac{n_i^2+n_in_e-n_e^2}{n_i+n_e}$ | 160 | $8 . 10^3$ | $5 . 10^4$ | $2 . 10^5$ | $7 . 10^5$ | $4 . 10^5$ |
| $n'$ | 164 | $8 . 10^3$ | $8 . 10^4$ | $3 . 10^5$ | $8 . 10^5$ | $5·5 . 10^5$ |

| Height (km.) | 160 | 170 | 180 | 190 | 200 |
|---|---|---|---|---|---|
| $(1-K_e)\dfrac{n_e^2}{n_i+n_e}$ | $8 . 10^4$ | $6 . 10^4$ | $2·5 . 10^4$ | $1·5 . 10^4$ | $6 . 10^3$ |
| $(1-K_i)\dfrac{n_i^2+n_in_e-n_e^2}{n_i+n_e}$ | $2 . 10^5$ | $6 . 10^4$ | $2·5 . 10^4$ | $1·5 . 10^4$ | $6 . 10^3$ |
| $n'$ | $3 . 10^5$ | $1·2 . 10^5$ | $5 . 10^4$ | $3 . 10^4$ | $1·2 . 10^4$ |

The resulting value of $N'\left(\equiv \int n'\,dh\right)$ is $2·3 . 10^{12}$, of which one-quarter is due to the electrons; it is slightly less than the estimate of $N_d$ ($4 . 10^{12}$—§ 9) the effective number of diamagnetic free charges.

This value of N′, by (34), shows that at the equator at noon, if Pedersen's values of $n_e$ and $n_i$ are correct, $I\left(\equiv -\int i\,dh\right) = 4 . 10^{-7}$ e.m.u. This is about 1/50 of the equatorial current-intensity associated with S, so that the free charges in and above the conducting layer affect the earth's field far more by their drift-motion than by their diamagnetism. It will be shown that if $N' = 2 . 10^{14}$, or about 100 times the number according to Pedersen, the drift-currents are capable of producing a diurnal magnetic variation very similar to S.

18. In both the dynamo and diamagnetic theories of S, it is supposed that

$n_e$ and $n_i$, or the quantities $\sigma$, $N_d$ which depend on them, are greatest at noon at the equator (considering the equinoctial season, for simplicity) and decrease with increasing zenith distance of the sun. The same reasonable assumption applies to N′, on which the total drift-current intensity I depends; this may be indicated by writing N′ as N′ $(\theta, \phi)$, where $\phi$ denotes local time, or longitude measured eastward from the midnight meridian. Hence

$$\mathrm{I}(\theta, \phi) = -\int i\,dh = \frac{m_i g}{\mathrm{H}_0}\mathrm{N}'(\theta, \phi)\frac{\sin\theta}{1 + 3\cos^2\theta}.$$

Let I $(\theta)$ denote the mean value of I $(\theta, \phi)$ round a circle of colatitude $\theta$, *i.e.*,

$$2\pi\mathrm{I}(\theta) = \int \mathrm{I}(\theta, \phi)\,d\phi.$$

Let

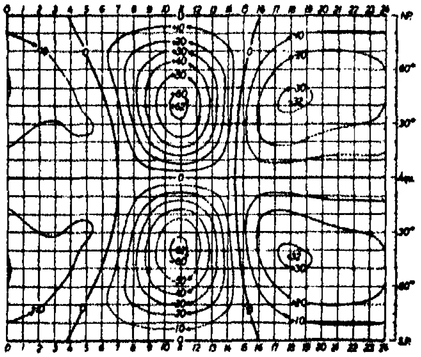
$$\mathrm{I}(\theta, \phi) = \mathrm{I}(\theta) + \Delta\mathrm{I}(\theta, \phi).$$

The term I $(\theta)$ denotes the mean eastward total drift-current intensity round the circle of colatitude $\theta$; this part satisfies the equation of continuity, and affects the daily mean value of the north and vertical components of H, but does not contribute to S. The term $\Delta$I $(\theta, \phi)$ denotes the difference between the local and the mean current-intensity in this latitude; this part will not satisfy the equation of continuity, but will tend to produce an accumulation of charge at the rate $-d\mathrm{I}(\theta, \phi)/a \sin\theta d\phi$, where $a$ denotes the earth's radius, or rather that of the ionised layer; the rate of accumulation of charge is here reckoned per square centimetre area of a vertical column. Since I increases towards noon, and decreases after noon, positive charge tends to accumulate over the post meridiem hemisphere, and negative over the ante meridiem hemisphere.

Any accumulation of charge would set up potential differences opposing the accumulation, and tending to equalise the drift-current in each latitude. But owing to the long free paths of the charges in the drift-current layer, a potential gradient along the circles of latitude, that is, transverse to the magnetic meridians, will have little direct effect in opposing the accumulations; instead of this it would tend to make both the positive and negative charges move upwards* or downwards normal to the magnetic field. But the medium is highly conducting along the lines of force, and electricity can flow freely in this direction to or from the conducting layer below; the drift-current layer is, as it were, connected to the conducting layer by a sheaf of laterally insulated conductors lying along the lines of force. Hence no serious accumulation of

* Upwards over the sunlit hemisphere.

charge can be set up, because this would produce large potential gradients not only in the drift-current layer, but also in the conducting layer below. Thus the drift-currents would produce closed electrical circuits partly traversing the conducting layer; charge would accumulate until the potential gradient just enabled the current, the amount of which is determined by the value of N′ in the drift-current layer, to overcome the resistance of the remainder of the circuit. The resultant current-system would resemble that shown in the figure, except that the current foci would be on the noon meridian, or slightly later, where N′ has its maximum value.



Over the night hemisphere the drift-current $\Delta I(\theta, \phi)$ is westward, as in fig. 1, but the whole current $I(\theta, \phi)$ is everywhere eastward. Hence $I(\theta)$ must at least equal the maximum westward value of $\Delta I(\theta, \phi)$, so that the noon current $I(\theta) + \Delta I(\theta, \phi)$ must be not less than the numerical sum of the maximum eastward and westward current-intensities in the day and night hemispheres; this is approximately $3 \cdot 10^{-5}$ e.m.u. (§ 1). The value of N′ required to make $I_{\text{max.}} = 3 \cdot 10^{-5}$ is $2 \cdot 10^{14}$, or about 1/250 times the number required by the diamagnetic theory. It therefore seems clear that the diamagnetism can account for at most less than 1 per cent. of S.

19. The positive ions will move eastward and the negative ions and electrons will move westwards, with velocities lying between 5 and 15 cm./sec. It may be shown that these opposing drifts will scarcely affect the distribution of the various kinds of charge, when the processes of ionisation and recombination are taken into account. Consider, for example, the change of $n_+$; the equation is

$$\frac{\partial n_+}{\partial t} = \beta - \alpha_{+-} n_+ n_- - \alpha_{+e} n_+ n_e - \frac{\partial (n_+ V_+)}{a \sin \theta \, \partial \phi},$$

where $\beta$ denotes the rate of formation of ions per cubic centimetre, and the $\alpha$'s are coefficients of recombination, while the last term represents the rate of accumulation owing to the drift of the ions; $V_+$ is independent of $\phi$. We may replace $\partial/\partial t$ by $\partial/\partial\phi$, reckoning $\phi$ in time-units (seconds); if $\phi$ is thus reckoned also in the last term, where as written it is supposed reckoned in circular measure, we must multiply the last term by $86{,}400/\pi$. Hence the equation may be written

$$\left(1 + \frac{8 \cdot 64 \,.\, 10^4}{2\pi a \sin \theta} V_+\right) \frac{\partial n_+}{\partial \phi} = \beta - \alpha_{+-} n_+ n_- - \alpha_{+e} n_+ n_e.$$

Since $V_+$ is of order 10, while $a = 6 \cdot 8 \,.\, 10^8$, the first factor on the left differs from 1 by only $2 \,.\, 10^{-4}$, which is negligible. Thus the drift has only a minute proportional influence on the distribution of the positive ions (and likewise for the negative ions and electrons), which will be most numerous on or near the noon meridian.

20. The type of S and its current-system can be explained either by the dynamo theory, or by the diamagnetic theory of Ross Gunn, or by the hypothesis (the "drift-current theory") that the drift-currents are the main cause.

The diamagnetic and drift-current theories are more definite than the dynamo theory, because they depend only on the distribution of ions and electrons in the upper atmosphere, while the dynamo theory involves this and also the unknown convective motion of the upper air. The two former theories imply that the S-current foci should be on or slightly after the noon meridian, instead of 1 or 1¼ hour before, as the observations indicate. The dynamo theory is not committed to any definite prediction of the phase, so long as we remain ignorant of the convective motion in the upper atmosphere; but in so far as the attempt has been made, first by Schuster and then, rather differently, by the writer, to connect these motions with those observed in the lower atmosphere, the result has not been entirely favourable to the dynamo theory. Schuster considered both the diurnal and semidiurnal atmospheric motions as indicated by the barometer, and found that, taking self-induction into account, the predicted variations were from 2 to 2¾ hours later than the observed; the writer, considering only the fundamental semidiurnal oscillation, found a similar phase difference between the prediction and observations. The discrepancy is therefore about twice as great as on the drift-current hypothesis.

If, as I have recently suggested, the convective motion is an independent one associated with a large diurnal variation of temperature in the upper atmosphere, and if the corresponding pressure variation is not complicated by resonance, but has its maximum at the same time as the temperature, then the current foci for the circuit which is eastward at the equator should be on or after the 18h meridian. Thus the phase of S constitutes a real difficulty in all the three theories, and possibly most of all for the dynamo theory.

It may, however, be possible to explain the phase of S by the dynamo theory, if it can be shown that there is an inversion or large change of phase of the upper-atmospheric diurnal convection. Alternatively, S may be mainly due to drift-currents, but also partly to dynamo-action, the latter being called upon to account for the advance of the current-foci from noon to about 11h ; this hypothesis likewise requires a complete or partial inversion of the high-level diurnal convection. The second of these theories may be called the "drift + dynamo" hypothesis. Because of the definite small discrepancy of phase, it does not seem possible to account for S by drift-currents alone.

21. The ultimate choice between the various proposed theories will depend largely on the determination of the distribution of ions and electrons in the upper atmosphere. The drift-current and diamagnetic theories are concerned mainly with the diurnal variation in this distribution ; they would be unaffected by a layer in which the electron or ion content, however great, was constant throughout the day and night. The dynamo theory, on the other hand, would be affected by an addition of conductivity uniform throughout the 24 hours ; however, the radio evidence suggests that in the layer, from 100 to about 170 km., where the main conductivity exists, the free charges are much reduced by the recombination during the night.

Since the number of free charges cannot be negative, the minimum values of $N_d$ or $N'$ at the equator at noon required to explain S by the drift-current or diamagnetic theories are equal to the difference between the midnight and noon values of N ; as has been seen, they are approximately $5 . 10^{16}$ and $2 . 10^{14}$. Since $N_d$ and $N'$ must be nearly equal, by their definition, it is clear that if $N_d$ were $5 . 10^{16}$, the drift-currents would be great enough to produce a diurnal magnetic variation 250 times as intense as is observed. This consideration is fatal to the diamagnetic theory, despite its attractive character from a qualitative standpoint. It seems possible to conclude that the diamagnetism of the outer atmosphere makes only an insignificant contribution to S.

Further, unless we are to admit the unlikely hypothesis that S is due to two or more independent causes producing effects which nearly balance one another, it seems possible to conclude that the difference between the noon maximum and night minimum of $N'$ on the equator cannot exceed $2 . 10^{14}$.

The diamagnetic theory having been eliminated, the choice seems narrowed down to the dynamo theory, or the "drift + dynamo" theory. The latter can be excluded if it can be shown that in the actual atmosphere the difference between the noon maximum and night minimum of N′ on the equator is much smaller than $2 . 10^{14}$ (*e.g.*, only one-tenth as great); if, however, this difference is shown to be about equal to $2 . 10^{14}$, the drift theory will be substantially confirmed,* but the dynamo theory must probably still be called upon to account for the advance of phase. The dynamo theory will remain a possible explanation either of the major part of S, or of an appreciable fraction of S (in *conjunction with the drift-currents as the major cause*), unless both the conductivity of the layer, and the phase or intensity of the diurnal convection, can be proved inadequate.

22. Besides setting an upper limit to the diurnal variation of N′, the magnetic observations place a restriction upon its mean value, because the latter affects the part of the earth's mean magnetic field which is due to external causes. The various spherical harmonic analyses of the field have shown that the external portion is only a small fraction of the whole, too small, indeed, to be inferred at all accurately from the magnetic data. This implies that the earth's magnetic field above the ionised atmosphere is nearly the same as if the atmosphere were absent; in this respect the earth is very different from the sun, whose atmosphere almost completely imprisons the internal magnetic field, so that no lines of force extend beyond the drift current layer existing in and below the reversing layer.†

According to L. A. Bauer's analysis of the earth's field, for 1922, the part of the field of external origin is directed northwards and upwards (in the northern hemisphere), the horizontal component at the equator being about $450\gamma$; this corresponds to a current-intensity I in the atmosphere of $5 \cdot 4 . 10^{-4}$ e.m.u., or, if the currents are supposed to be "drift-currents," to a mean equatorial value $6 \cdot 6 . 10^{15}$ for N′. This may be taken as an upper limit of the mean value of N′ round the equator.

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* In this case the general discussion of the current-system given in § 18 must be supplemented by a mathematical investigation.

† Chapman, 'M.N.R.A.S.,' vol. 89, p. 57 (1928).

# *The Vertical Force on a Cylinder Submerged in a Uniform Stream.*

By T. H. Havelock, F.R.S.

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1. The horizontal force on a circular cylinder immersed in a stream is familiar as an example of wave resistance. The following note supplies a similar calculation for the resultant vertical force. The problem was suggested in a consideration of the forces on a floating body in motion, the horizontal and vertical forces and the turning moment; but the case of a partially immersed body presents great difficulties. It seemed, however, of sufficient interest to compare the resultant horizontal and vertical forces for a simple case of complete immersion for which the calculations can be carried out. The horizontal force, or wave resistance, has usually been obtained indirectly from considerations of energy, but a different method is adopted here for both components of force and the turning moment. In a former paper the method of successive images was applied to the problem of the circular cylinder, taking images alternately in the surface of the cylinder and in the free surface of the stream. Using these results to the required stage of approximation, the complete force on the cylinder is now obtained as the resultant of forces between the sources and sinks within the cylinder and those external to it. The same method can be applied to any submerged body for which the image sytems are known, and the resultant force and couple calculated in the same manner.

The proposition used in this method is that for a body in a fluid, the motion of which is due to given sources and sinks, the resultant force and couple on the body are the same as if the sources and their images attract in pairs according to a simple law of force, inverse distance for the two-dimensional case and inverse square of the distance for point sources. This fairly obvious proposition follows directly from a contour integration in the two-dimensional case; and, in view of the application, the extension is given in § 2 when the flow is due to a distribution of doublets. In § 3 the horizontal and vertical force on a circular cylinder are obtained by this method, the former agreeing with the usual expression for the wave resistance. The different variation of the two components with velocity is of interest, and the expressions are graphed on the same scale. The additional vertical force due to velocity changes direction at a certain speed, and is clearly associated more with the surface elevation immediately over the centre of the cylinder. In § 4 reference is made to the couple on the cylinder. This should, of course, be zero for a complete solution; it is verified that the method used here gives zero moment up to the stage of approximation in terms of the ratio of the radius of the cylinder to the depth of its centre.

2. Consider steady two-dimensional flow of a liquid of density $\rho$ past a solid body, the motion being irrotational and there being no field of force. The motion being specified in the usual manner by a function $w$ of the complex variable $x+iy$, the resultant force (X, Y) on the solid and the moment M about the origin are given by

$$X - iY = \tfrac{1}{2}\rho i \int \left(\frac{dw}{dz}\right)^2 dz, \tag{1}$$

$$M = -\tfrac{1}{2}\rho \int z \left(\frac{dw}{dz}\right)^2 dz, \tag{2}$$

where in (2) the real part is to be taken. In each case the integration is taken round the contour of the rigid body, or indeed round any contour enclosing the body but excluding any external sources and sinks.

Now suppose the motion to be given by

$$w = -\Sigma m_r \log(z - z_r) - \Sigma m_s \log(z - z_s), \tag{3}$$

where the suffix $s$ refers to the given distribution in the liquid, and $r$ to the image system within the surface of the body, $m_r$ and $m_s$ being real.

Forming $(dw/dz)^2$, we see that this quantity has simple poles at the points $z_r$ within the contour of integration: and we obtain at once from the theory of residues

$$X - iY = -2\pi\rho\, \Sigma \frac{m_r m_s}{z_r - z_s}, \tag{4}$$

the summation extending over the external and internal sources taken in pairs. Hence we obtain

$$X = 2\pi\rho\, \Sigma m_r m_s (x_s - x_r)/R_{rs}^2,$$
$$Y = 2\pi\rho\, \Sigma m_r m_s (y_s - y_r)/R_{rs}^2. \tag{5}$$

It follows that the resultant force is the same as if each pair of external and internal sources attracted each other with a force $2\pi\rho m_r m_s/R_{rs}$, where $R_{rs}$ is the distance between them.

It may easily be verified in the same way from (2) that the moment M is accounted for by the same forces acting at the internal sources. It is convenient to have a similar analysis for doublets. If M is the moment of a doublet making an angle $\alpha$ with the axis of $x$, we have with the same notation as before,

$$w = \Sigma \frac{M_r e^{i\alpha_r}}{z - z_r} + \Sigma \frac{M_s e^{i\alpha_s}}{z - z_s}. \tag{6}$$

Forming $(dw/dz)^2$ we see that again the only terms which give any contribution to the integral (1) are the product terms in $r$ and $s$, and for a typical term we have

$$\int \frac{dz}{(z - z_r)^2 (z - z_s)^2} = -\frac{4\pi i}{(z_r - z_s)^3}. \tag{7}$$

Thus we obtain

$$X - iY = -4\pi\rho \Sigma \frac{M_r M_s e^{i(\alpha_r + \alpha_s)}}{(z_s - z_r)^3}. \tag{8}$$

and the contribution to the total force due to $M_r$ and $M_s$ is

$$\begin{aligned} X_{rs} &= -4\pi\rho M_r M_s \cos(\alpha_r + \alpha_s - 3\theta_{rs}) / R_{rs}^3, \\ Y_{rs} &= 4\pi\rho M_r M_s \sin(\alpha_r + \alpha_s - 3\theta_{rs}) / R_{rs}^3, \end{aligned} \tag{9}$$

$\theta_{rs}$ being the angle between $Ox$ and the vector $R_{rs}$ drawn from the doublet $(r)$ to the doublet $(s)$. Further, calculating the total moment M from (2), the product terms $M_r M_s$ are the only terms which give any value, and the corresponding contour integral is

$$\int \frac{z\,dz}{(z - z_r)^2 (z - z_s)^2} = 2\pi i \frac{z_r + z_s}{(z_s - z_r)^3}. \tag{10}$$

Hence we obtain

$$M = -2\pi\rho i \Sigma M_r M_s e^{i(\alpha_r + \alpha_s)} (z_r + z_s)(z_s - z_r)^{-3}, \tag{11}$$

the real part to be taken.

On reduction it is seen that this consists of the sum of the moments of the forces given by (9) acting at the internal doublets, together with a couple for each pair of internal and external doublets of amount

$$2\pi\rho M_r M_s \sin(\alpha_r + \alpha_s - 2\theta_{rs}) \,.\, / R_{rs}^2. \tag{12}$$

The contribution to the forces and moment on the body when the external field includes also a uniform flow can easily be obtained in the same manner.

3. We now apply these expressions to a circular cylinder of radius $a$ submerged in a uniform stream. Take $Ox$ in the undisturbed surface of the stream, $Oy$ vertically upwards; and let the stream velocity be $c$ in the negative direction of $Ox$. Let the centre C of the circle be at the point $(0, -f)$. Then the image of the stream in the circle is a horizontal doublet at C of moment $ca^2$. The

image system of this doublet in the free surface of the stream consists of a horizontal doublet of moment $-ca^2$ at $C_1$ the image point $(0, f)$, together with a continuous line distribution of doublets along a horizontal line through $C_1$ in the negative direction of $Ox$. At a point $(-p, f)$ on this line the moment of an elementary doublet is $2\kappa_0 ca^2 dp$, where $\kappa_0 = g/c^2$, and the axis of the doublet makes an angle $\kappa_0 p - \frac{1}{2}\pi$ with the positive direction of $Ox$.* We may stop at this stage meantime.

In the notation of the previous section the external system $(s)$ consists of the uniform stream and the image system just specified; the internal system $(r)$ is the doublet $ca^2$ at the point $(0, -f)$.

For the wave resistance R, we have from (9)

$$R = -X = 8\pi\rho\kappa_0 c^2 a^4 \int_0^\infty \frac{\cos(\kappa_0 p - \frac{1}{2}\pi - 3\theta)}{(p^2 + 4f^2)^{3/2}}\, dp, \tag{13}$$

where

$$\sin\theta = 2f/(p^2 + 4f^2)^{\frac{1}{2}}; \quad \cos\theta = -p/(p^2 + 4f^2)^{\frac{1}{2}}.$$

This gives

$$R = -8\pi\rho\kappa_0 c^2 a^4 \int_0^\infty \frac{p(p^2 - 12f^2)\sin\kappa_0 p + 2f(3p^2 - 4f^2)\cos\kappa_0 p}{(p^2 + 4f^2)^3}\, dp. \tag{14}$$

This integral may be derived from

$$\int_0^\infty \frac{p\sin\kappa_0 p + 2f\cos\kappa_0 p}{p^2 + 4f^2}\, dp = \pi e^{-2\kappa_0 f}, \tag{15}$$

by differentiating twice with respect to $f$; and we obtain

$$R = 4\pi^2 g\rho\kappa_0^2 a^4 e^{-2\kappa_0 f}, \tag{16}$$

in agreement with other methods.

Turning to the vertical force, if we calculate it from the expressions in (9) we shall obtain the hydrodynamic part depending upon the velocity. There is also the hydrostatic part $g\rho\pi a^2$, arising from the term $g\rho y$ in the expression for the pressure; and in addition there is the weight of the cylinder itself. We may assume the cylinder to be of the same density as the liquid, and then the calculation will give the total vertical force.

Measuring Y vertically upwards, the contribution of the two finite doublets at C and $C_1$ is, from (9),

$$-\pi\rho c^2 a^4/2f^3. \tag{17}$$

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* 'Roy. Soc. Proc.,' A, vol. 115, p. 271 (1927).

The part arising from the interaction of the line distribution of doublets and the doublet at C is

$$8\pi\rho\kappa_0 c^2 a^4 \int_0^\infty \frac{\sin(\kappa_0 p - \frac{1}{2}\pi - 3\theta)}{(p^2 + 4f^2)^{3/2}}\, dp, \tag{18}$$

which reduces to

$$8\pi\rho\kappa_0 c^2 a^4 \int_0^\infty \frac{p(p^2 - 12f^2)\cos\kappa_0 p - 2f(3p^2 - 4f^2)\sin\kappa_0 p}{(p^2 + 4f^2)^3}\, dp. \tag{19}$$

This integral may be evaluated by differentiating twice with respect to $f$ the integral

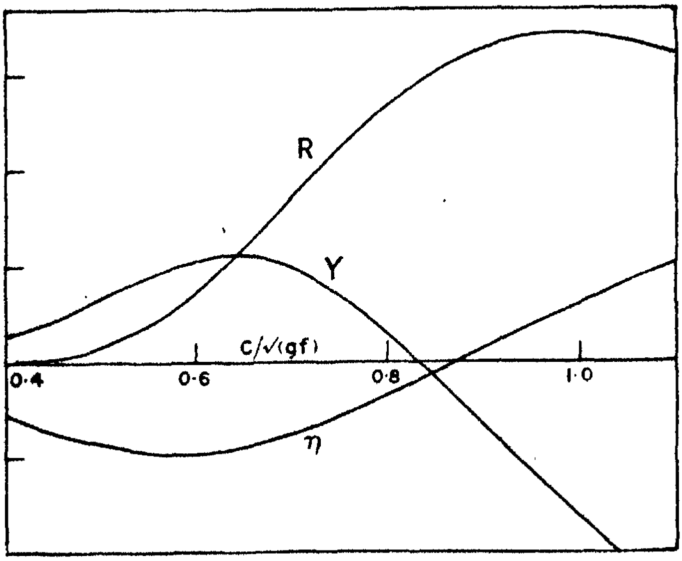
$$\int_0^\infty \frac{p\cos\kappa_0 p - 2f\sin\kappa_0 p}{p^2 + 4f^2}\, dp = -e^{-2\kappa_0 f}\, li\,(e^{\kappa_0 f}), \tag{20}$$

where $li$ is the logarithmic integral.

Collecting the terms from (17) and (19) we obtain finally

$$Y = -\frac{\pi\rho c^2 a^4}{2f^3}\{1 + 2\kappa_0 f + 4\kappa_0^2 f^2 - 8\kappa_0^3 f^3 e^{-2\kappa_0 f}\, li\,(e^{2\kappa_0 f})\}. \tag{21}$$

This vertical force changes from upwards to downwards at a certain velocity. For when $c$ is small, that is $\kappa_0 f$ large, using the asymptotic expansion of the logarithmic integral we find that Y approximates to $\pi\rho c^2 a^4/2f^3$; on the other hand, when $c$ is large, Y is approximately $-\pi\rho c^2 a^4/2f^3$. The value of (21) can be calculated readily from tables and it is of interest to compare the relative values of R and Y and their variation with velocity.



The figure shows R and Y graphed on the same scale on a base of $c/\sqrt{(gf)}$. R is very small at low velocities and then increases rapidly to its maximum at about $c = \sqrt{(gf)}$. On the other hand Y is relatively large at lower velocities, and changes sign at about $c = 0 \cdot 84 \sqrt{(gf)}$. The wave resistance arises from the flow of energy in the regular waves to the rear of the cylinder, while the vertical force is associated more with the surface elevation near the cylinder. The surface elevation immediately above the centre of the cylinder is given by*

$$\eta = (2a^2/f)\{1 - \kappa_0 f e^{-\kappa_0 f} \, li \, (e^{\kappa_0 f})\}, \tag{22}$$

and for comparison this is shown on the figure with an arbitrary scale for the ordinates. Doubtless the variation in the vertical force with the velocity is connected with the mean curvature of the lines of flow in the neighbourhood of the cylinder. It may be noted that the usual approximation for the pressure condition at the free surface involves neglecting the square of the slope of the surface; this would not affect the present approximation but would come into the next stage involving higher powers of the ratio $a/f$.

4. Obviously in a complete solution the fluid pressures on the cylinder cannot give rise to any couple. As the method of successive images amounts to an expansion of the solution in ascending powers of $a/f$, it is worth while verifying that the couple is zero at each stage of the approximation. With the images specified up to the present the couple comes from the interaction of the doublet at C with the line distribution to the rear of $C_1$. Using the result (12), this gives a moment

$$4\pi\kappa_0\rho c^2 a^4 \int_0^\infty \frac{\sin(\kappa_0 p - \frac{1}{2}\pi - 2\theta)}{p^2 + 4f^2}\, dp, \tag{23}$$

which, on substituting for $\theta$, gives

$$4\pi\kappa_0\rho c^2 a^4 \int_0^\infty \frac{4pf \sin \kappa_0 p - (p^2 - 4f^2)\cos \kappa_0 p}{(p^2 + 4f^2)^2}\, dp. \tag{24}$$

This can be evaluated, and its value is not zero. But it can be seen that we shall get a contribution of the same order, in the radius $a$, from the next stage of successive images. The next set of images is internal to the cylinder and consists of a horizontal doublet of moment $-ca^4/4f^2$ at the inverse point $C_2$ whose co-ordinates are $(0, -f + a^2/2f)$, together with a continuous distribution of doublets on a semi-circle described on $CC_2$ as diameter. At a point on this semi-circle whose co-ordinates are

$$-\frac{a^2 p}{p^2 + 4f^2}, \quad -f + \frac{2a^2 f}{p^2 + 4f^2},$$

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* 'Roy. Soc. Proc.,' A, vol. 121, p. 517 (1928).

the moment of an elementary doublet is $2\kappa_0 ca^4\,dp/(p^2+4f^2)$, and its axis makes with $Ox$ an angle

$$2\tan^{-1}(p/2f)-\kappa_0 p+\tfrac{1}{2}\pi.$$

Now at this stage the only additional terms of order $a^4$ for the turning moment arise from the interaction of the external uniform stream and the semi-circular distribution of doublets just described.

It can easily be seen that the amount due to the uniform stream and an internal doublet of moment $M_r$ at an angle $\alpha_r$ to $Ox$ is

$$-2\pi c\rho M_r\sin\alpha_r.$$

Therefore the additional couple of the specified order is

$$-4\pi\kappa_0\rho c^2 a^4\int_0^\infty\frac{\sin\{2\tan^{-1}(p/2f)-\kappa_0 p+2\pi\}}{p^2+4f^2}\,dp \qquad (25)$$

On reduction (25) comes to precisely the expression (24) with a minus sign and therefore the couple on the cylinder is zero to the order specified.

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# *The Photosynthesis of Naturally Occurring Compounds.* IV.—*The Temperature Coefficient of the Photosynthesis of Carbohydrates from Carbonic Acid.*

By E. C. C. Baly, F.R.S., and N. R. Hood, Liverpool University.

(Received October 4, 1928.)

The photosynthesis of carbohydrates from carbonic acid was described a short time ago in three communications,* the method being the irradiation with visible light of carbonic acid adsorbed on finely divided nickel and cobalt carbonates suspended in water. It was pointed out that the carbonates must be free from every trace of adsorbed alkali, this result being difficult to secure when these salts are prepared by the method of precipitation.

We have recently succeeded in developing a method whereby nickel carbonate can be prepared free from every trace of adsorbed salts. The method consists in the electrolysis of pure conductivity water, saturated with carbon dioxide, with nickel electrodes. A convenient form of apparatus may be made from a rectangular glass vessel with internal dimensions of 8 × 6 inches and 8 inches deep. The cell is provided with a wooden cover to which are attached three nickel plates 8 × 5 inches and ⅛-inch thick. One electrode is fixed at each end of the cell and one in the centre, the two outside electrodes being connected together. Two cooling coils are also attached to the cover, one on each side of the central electrode, and a stream of water is maintained through them. The cell is filled with conductivity water to within 1 inch of the top of the cell and a stream of pure carbon dioxide is continuously passed into the water. The electrodes are connected with a 230-volt circuit and sufficient resistance is intercalated to reduce the current to from 2·2 to 2·0 amperes. Since the area of each electrode immersed is 35 square inches the current density is about 1 ampere per square decimetre.

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* 'Roy. Soc. Proc.,' A, vol. 116, pp. 197, 212, 219 (1927).

The nickel carbonate falls to the bottom of the cell and about 30 grams may be obtained each day. Whilst the compound is necessarily free from alkali, it contains a little black oxide, which, however, has no effect on its efficiency in the photosynthetic reaction. Before use, however, the material has to be activated and the following procedure is adopted. After being collected the carbonate is dried at 100° and subsequently heated at 140° for 30 minutes. It is then powdered and passed through a 100-mesh sieve. As was described in Part II, the activation may be effected by exposure to light and the method at present in use is as follows. A very thin layer of the powder is evenly distributed by means of the 100-mesh sieve over a sheet of plate glass with area of about 5 square feet. On this glass sheet rests a light wooden frame about 2 inches deep and a second sheet of glass is laid thereon in order to protect the powder from contamination by dust. The layer of carbonate is irradiated on both sides, three 100-watt lamps being placed above and below the apparatus. Complete activation requires about 6 hours, but no harm is done by irradiation for 18 hours. The material must be used within a short time after activation.

The nickel carbonate prepared in the above way gives remarkably constant yields of carbohydrates when the temperature, light intensity and relation between volume of water and weight of powder are kept constant. The experimental accuracy now reached has enabled us to determine the yield of carbohydrates obtained at different temperatures, the remaining conditions being kept constant, and in Table I are given the amounts which were obtained at the specified temperatures with 50 grams of the carbonate suspended in 1500 c.c. of water, the total area of the exposed surface of the containing vessels being 360 sq. cm.

Table I.

| Temperature. | Yield of carbohydrates. | Temperature. | Yield of carbohydrates. |
|---|---|---|---|
| ° | grm. | ° | grm. |
| 5 | 0·0101 | 26 | 0·0648 |
| 11·5 | 0·0281 | 31 | 0·0783 |
| 17 | 0·0412 | 36 | 0·0238 |
| 21 | 0·0512 | 41 | 0·0061 |

The yields plotted against the temperature are shown by the full line in fig. 1, and, as can be seen, the relation is a linear one between 5° and 31°, and there is a very rapid decrease in yield when the temperature is increased above 31°.

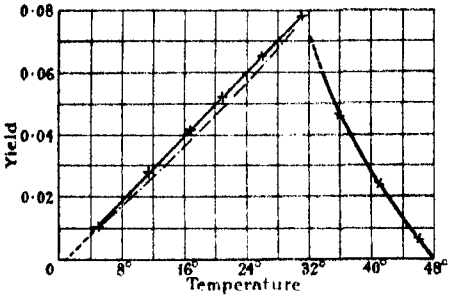

FIG. 1.

It should be explained that the yield of carbohydrates given is the actual weight of photosynthesised organic matter which is soluble in absolute methyl alcohol. We describe these products as carbohydrates for two reasons. In the first place they give the four reactions described in one of the previous papers.* In the second place they are similar in all their properties to the products obtained by the action of ultra-violet light on formaldehyde in aqueous solution. These latter products have been very fully investigated by the method of oxidation by means of bromine to the acids which have been separated and identified. The presence of glucose and fructose has been proved completely and the presence has also been proved of more complex carbohydrates which give hexoses on hydrolysis with cold dilute acid. The nature of these complex carbohydrates seems to depend on the hydrogen ion concentration during photosynthesis, and their investigation is not yet complete.

The linear relation between 5° and 31° shown in fig. 1 is of considerable interest in view of the fact that pure photochemical reactions have no temperature coefficient. It is also of interest because of the remarkable analogy it shows with the photosynthetic process *in vivo*. This analogy may be discussed in some detail.

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* *Loc. cit.*, p. 215.

In the first place, the values of the temperature coefficient for 10° ($Q_{10}$) may be compared with those found by Warburg with the unicellular alga *Chlorella** under constant illumination. The values calculated from fig. 1 and those given by Warburg are set forth in Table II.

Table II.

| | | | |
|---|---|---|---|
| Temperature range | 5° to 10° | 10° to 20° | 20° to 30° |
| $Q_{10}$ (B. and H.) | 4·50 | 2·11 | 1·54 |
| $Q_{10}$ (Warburg) | 4·3 | 2·1 | 1·6 |

The close similarity between the temperature coefficients of the photosynthesis in the living alga and in the inorganic process is very striking.

In the second place it is well known that in the vegetable kingdom there exists an optimum temperature for photosynthesis and that above this temperature the photosynthetic velocity rapidly declines. The phenomenon has been investigated by many botanists and reference in particular may be made to an admirable research by Miss Matthaei at Cambridge.† The method adopted was the determination of the maximum amounts of carbon dioxide assimilated at various temperatures and the relation between the two is shown in fig. 2, which has been redrawn from Miss Matthaei's values.

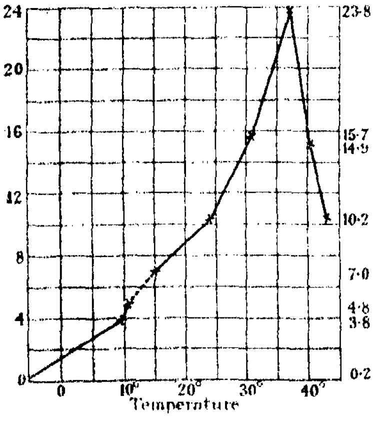

Fig. 2.

It may be seen that there is close similarity between the natural and laboratory processes, but there are certain differences between them which may be referred to. In the first place, the relation found by Miss Matthaei between temperature and carbon dioxide assimilated is not linear. This might at first sight appear to be an important divergence between the two processes, but it must be remembered that the determination of the carbon dioxide taken up by the leaves is not as accurate a measure of the amount of photosynthesis as the determination of the quantity of photosynthesised material. Then again, the process in the living plant is a complex one, since, apart from any other reason, at least two photosynthetic reactions are taking place to give carbohydrates and nitrogenous compounds and these might conceivably have different temperature coefficients. Furthermore, the determination of the temperature by thermocouples placed in the leaf tissue is less easy to control than in the case of the laboratory process. In this connection it is to be noted that Warburg, in the case of the alga *Chlorella*, where the temperature was under better control, found that the relation between temperature and photosynthesis was very nearly linear. This is shown by the values of the temperature coefficient given in Table II, and still more clearly by the dot and dash line in fig. 1, which expresses the Warburg relation and has been calculated from his temperature coefficients and our value at 5° as the origin. Lastly, it cannot be assumed that the orientation of the chloroplasts to the light remains constant at all temperatures. It is well known that this orientation changes when the light intensity changes, the tendency being to expose a smaller area to greater intensity of light. If the photosynthetic efficiency is increased by rise in temperature, it seems possible that this tendency may be decreased and, if that be so, the relation between photosynthesis and temperature will increasingly depart from linearity in the sense found by Miss Matthaei.

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* 'Biochem. Z.,' vol. 100, p. 258 (1919).

† 'Phil. Trans.,' B, vol. 197, p. 47 (1905).

It may be concluded, therefore, that Miss Matthaei's results do not prove that the relation between temperature and a single photosynthetic process is not a linear one.

Perhaps the most remarkable fact that has been established is that the photosynthetic process, both in the living leaf and in the laboratory, has an upper and a lower temperature limit. It is true that Miss Matthaei found in the living leaf that the upper temperature limit is about 5° higher and that the lower temperature limit is about 5° lower than in the laboratory process, but this may well be due to the difference between the adsorbing surfaces in the two cases.

The more rapid decline in photosynthetic velocity in the living leaf when the temperature is raised above the upper limit is doubtless due to the same cause.

In the living process time has a very definite influence on the maximal rate of photosynthesis and in consequence of this plant physiologists, following the lead of Blackman,* have formed the opinion that two opposing reactions take place. On this view the existence of the upper temperature limit is due to the superposition of a second process, *e.g.*, the increasingly rapid de-activation of the chloroplasts with rise of temperature, on the first or true photosynthetic reaction. The results now recorded show, however, that both lower and upper temperature limits must be due to some fundamental cause which is characteristic of a simple photochemical surface reaction.

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* 'Ann. Botany,' vol. 19, p. 282 (1905).

We do not propose in this communication to discuss the physical explanation of the facts that have been observed in the laboratory process, but it may be pointed out that these give undoubted support to the view expressed in Part III that the complete activation of the carbonic acid is achieved in two stages, namely, partial activation by adsorption on the surface of the catalyst and a second activation by the action of visible light on the adsorbed layer. This view was based on the following facts :—

1. Carbonic acid is not acted on by white light.
2. Carbonic acid when adsorbed on a coloured surface does not react in the dark.
3. Carbonic acid when adsorbed on a coloured surface and irradiated by white light reacts to give carbohydrates.

   Since a pure photochemical reaction has no temperature coefficient it may be concluded that—
4. The number of partially activated molecules in the adsorbed layer which are able to enter into the final reaction is in linear proportion to the temperature between the limits of 1° and 31°.

It is possible that the first process, or partial activation by adsorption, corresponds to what is known as the Blackman reaction in the living plant.

# *The Equilibrium of Heterogeneous Systems including Electrolytes. Part* III.[*] *The Effect of an Electric Field on the Adsorption of Organic Molecules, and the Interpretation of Electro-capillary Curves.*

By J. A. V. Butler, D.Sc., University of Edinburgh.

(Communicated by Sir James Walker, F.R.S.—Received September 13, 1928.)

In an exhaustive series of researches, Gouy[†] examined the effect of the addition of organic substances on the electro-capillary curve of mercury in a solution of an inactive salt, such as sodium sulphate. He found that, with rare exceptions, these substances caused a depression of the curve which was greatest in the neighbourhood of its maximum, falling off on each side and, in many cases, ultimately becoming zero. He ascribed this behaviour to the effect of the electric field on the adsorption of the added substance, the amount adsorbed being greatest when the electric field at the interface is small and diminishing as the field increases in either direction.

A quantitative calculation of the effect was attempted by Frumkin.[‡] He obtained the work done in adsorption on account of the electric forces at the interface as the sum of two terms: (1) a general term, due to the smaller dielectric constant and greater length of the organic molecule, than water, which he evaluated as $\frac{1}{2}(c - c')\,\psi^2$, where $c$ is the capacity of the double layer per unit surface in the pure solvent, $c'$ that when the surface is saturated with the adsorbed substance, and $\psi$ the potential difference between the interface and the interior of the solution; (2) a term dependent on the dipole moment of the adsorbed molecule, given as $c'\psi_N\psi$, where $\psi_N$ is the potential difference due to the dipoles, between uncharged mercury and the solution when the surface of the former is completely covered with adsorbed molecules. He thus obtained the total work done by the electric forces in adsorption, which he wrote $\phi s$, and took their effect as equivalent to a dilution of the solution in the ratio $e^{\phi s/\mathrm{RT}}$. The effect of this apparent dilution on the surface tension was obtained by the use of somewhat complicated adsorption equations, but by their use Frumkin was able to account for the effect of amyl alcohol on the electrocapillary curve.

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[*] Part II, 'Roy. Soc. Proc.,' A, vol. 113, p. 594 (1927). The following corrections should be noted. The quotation (p. 597, line 1) describing R. K. Schofield's work, which might appear to be Dr. Schofield's own account, is from E. K. Rideal's "Surface Chemistry" ('Camb. Univ. Press,' 1926). P. 597, line 4: *for* $d\mu_{\mathrm{H}\ddot{\mathrm{g}}_s}$ *read* $\Gamma_{\mathrm{H}\ddot{\mathrm{g}}_s}$. P. 599, equation (6), p. 600, line 3, and p. 601, equation (12): *for* $a_{\mathrm{Hg}^+}\Gamma_{\mathrm{Hg}^+} + a_s\Gamma_s$ *read* $-(a_{\mathrm{Hg}^+}\Gamma_{\mathrm{Hg}^+} + a_s\Gamma_s)$; p. 601, equations (12) and (13): *for* $a_{\mathrm{Hg}^+}\Gamma'_{\mathrm{Hg}^+}$ *read* $-a_{\mathrm{Hg}^+}\Gamma'_{\mathrm{Hg}^+}$.

[†] 'Ann. Chim. Phys.,' vol. 29, p. 145 (1903), vol. 8, p. 291 (1906), and vol. 9, p. 75 (1906); 'Ann. Physique,' vol. 6, p. 5 (1916), and vol. 7, p. 129 (1917).

[‡] 'Z. Physik,' vol. 35, p. 792 (1926).

We shall take as our starting point the following equation obtained in the previous paper* for the surface tension of a polarised mercury surface in contact with an aqueous solution :—

$$\gamma = \sigma_0 - \int \Gamma_{\mathrm{Hg}^+} \,.\, d\mathrm{M}_{\mathrm{Hg}^+} - \int \Gamma_\epsilon \,.\, d\mathrm{M}_\epsilon - \int \Gamma_x \,.\, d\mathrm{M}_x \ldots - k\mathrm{V}^2 \quad (1)$$

Here $\sigma_0$ is the surface tension of uncharged mercury in the pure solvent; $\Gamma_{\mathrm{Hg}^+}$, $\Gamma_\epsilon$, $\Gamma_x$ are the excess amounts of mercury ions, electrons and any component X, when the interface is fixed as there defined; $\mathrm{M}_x$ is the chemical potential (or partial free energy) of the substance X in the solution, etc., and V the potential difference at the interface. The term $k\mathrm{V}^2$ gives the effect of the electric field itself on the surface tension.

The depression of the surface tension produced by the substance X is thus

$$\Delta\gamma = \int \Gamma_x \,.\, d\mathrm{M}_x. \quad (2)$$

If $\Gamma_x$ is a function of the potential difference V, we may put

$$\Gamma_x = \Gamma_0 \,.\, f(\mathrm{V}) \quad (3)$$

where $\Gamma_0$ is the amount adsorbed when $\mathrm{V} = 0$, so that

$$\Delta\gamma = \int \Gamma_0 \,.\, f(\mathrm{V}) \,.\, d\mathrm{M}_x.$$

Now, if it be taken that $f(\mathrm{V})$ is a function which does not involve $\mathrm{M}_x$, we have

$$\Delta\gamma = f(\mathrm{V}) \int \Gamma_0 \,.\, d\mathrm{M}_x,$$

and since $\int \Gamma_0 \,.\, d\mathrm{M}_x$ is the depression caused by X when $\mathrm{V} = 0$ (which may be written $\Delta\gamma_0$), we have

$$\Delta\gamma = \Delta\gamma_0 \,.\, f(\mathrm{V}) \quad (4)$$

We therefore need to know the form of the function $f(\mathrm{V})$.

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* 'Roy. Soc. Proc.,' A, vol. 113, p. 594 (1927).

### *The Effect of an Electric Field on the Adsorption of Molecules.*

We shall take as a basis the result obtained in electrostatic theory,* that the work done by an element of dielectric of volume $\delta v$, when it is moved from a place where the electric field is E to a place where the electric field is zero is

$$w = \delta v \,.\int \mathrm{P}\,.\,d\mathrm{E}, \tag{5}$$

where P is the polarisation per unit volume corresponding to the field strength E. Now in moderate fields P is proportional to E and we may write $\mathrm{P} = \alpha\mathrm{E}$, so that $w = \delta v \,.\, \frac{1}{2}\alpha\mathrm{E}^2$.

Consider now the distribution of molecules of two kinds A and B between a region I in a solution where the field strength is zero and a region II where the field strength is E. Let A be the solvent and B a solute present in relatively small concentration. When a molecule of B of volume $\delta v_{\mathrm{B}}$ is moved from region I to region II it displaces a quantity of A, occupying the same volume in the opposite direction. The work done against the electric forces acting on the molecules, in the transfer, is thus

$$w = \tfrac{1}{2}\,(\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})\,.\,\mathrm{E}^2\,.\,\delta v_{\mathrm{B}}, \tag{6}$$

where $\alpha_{\mathrm{A}}$ and $\alpha_{\mathrm{B}}$ are the appropriate values of $\alpha$ for the two substances. Thus if $n^0_{\mathrm{B}}$ be the number of molecules of B in a given volume of region I ($\mathrm{E} = 0$) and $n_{\mathrm{B}}$ that in region II (field strength, E) according to the Boltzmann distribution equation we have

$$n^0_{\mathrm{B}}\, e^{-\frac{1}{2}(\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}})\,\mathrm{E}^2\,.\,\delta v_{\mathrm{B}}/k\mathrm{T}} \tag{7}$$

which holds if $n_{\mathrm{B}}$ is relatively small.

The application of (7) to the calculation of the effect of an electric field on the amount of substance adsorbed at a mercury surface in contact with the solution presents certain difficulties. We may suppose that the solution contains an electrolyte, in addition to the substance B and that the potential difference between the mercury and the solution is kept at the value V by polarisation. Let the excess of B, present at the interface when $\mathrm{V} = 0$ be $\Gamma_0$. In order to find the value of $\Gamma$ for a given value of V, we should need to know how the adsorbed substance is distributed in the interface and also the electric field at each point, *i.e.*, the constitution of the electrical double layer. In the absence of this knowledge, we may assume that the whole amount adsorbed changed in the same proportion as that part of it which is nearest to the mercury surface, so that if E be the electric field at the surface of the mercury, we may put

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* Livens, "The Theory of Electricity," p. 82 (2nd ed., 'Camb. Univ. Press,' 1926).

$$\Gamma = \Gamma_0 \, e^{-\frac{1}{2}(\alpha_A - \alpha_B) \,.\, E^2 \,.\, \delta v_B / kT}. \tag{8}$$

Thus, by (3) and (4) the depression of the surface tension is

$$\Delta\gamma = (\Delta\gamma_0) \, e^{-\frac{1}{2}(\alpha_A - \alpha_B) \,.\, E^2 \,.\, \delta v_B / kT}$$

or substituting $E = \kappa V$, we have

$$\Delta\gamma = (\Delta\gamma_0) \, e^{-aV^2}, \tag{9}$$

where

$$a = \tfrac{1}{2} (\alpha_A - \alpha_B) \,.\, \kappa^2 \,.\, \delta v_B / kT. \tag{9A}$$

In a great majority of cases the variation of the depression of the surface tension with the potential difference is closely in accordance with an equation of this form. Thus, fig. 1 shows the depression of the surface tension produced by phenol (molar) in a solution of sodium sulphate (M/2), plotted against the applied potential difference.* If we put, provisionally $V = 0$ at the maximum of this curve, we find that the equation

$$\Delta\gamma = (\Delta\gamma_0) \, e^{-3 \cdot 23 V^2}$$

closely represents the observed results.

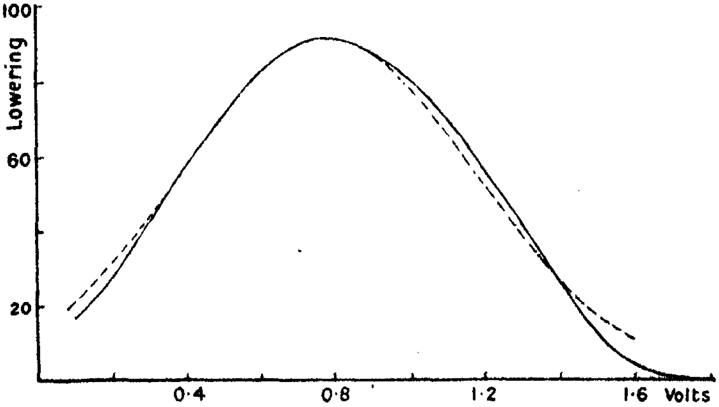

FIG. 1.—Adsorption Curve of Phenol (M/1). Surface tension lowering plotted againt applied potential difference in volts. ——— observed. - - - - - calculated.

### *The Effect of Orientation at the Interface.*

According to (9) the maximum of adsorption occurs when the potential difference between the mercury and the solution is zero. The exact position of this point is unknown. The identification of the maximum of the electrocapillary curve with the "null-point" was discredited by S. W. J. Smith and by Gouy,* because it occurs in different solutions at different points. This variation is probably to be ascribed to the adsorption of ions from the solution, and if we could obtain an electrocapillary curve unmodified by the adsorption of any component from the solution, it is reasonable to suppose that its maximum would correspond to the true "null-point." The maxima of the curves of "inactive" salt solutions come within a limited range and the null-point is probably in this vicinity.

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* We shall call this curve the *adsorption curve* of the substance.

Whether this is so or not, referred to the same standard electrode, the maxima of the adsorption curves should by (9) all occur at the same value of V. It is found, however, that while in nearly all cases these curves are of the general form of equation (9), the maximum is often displaced, sometimes considerably, to the right or left of the maximum of the primitive solution.

This behaviour can be accounted for if we suppose that the adsorbed molecules have a polarisation, $p$ per unit volume, in the absence of an electric field, arising from the orientation of their dipoles at the surface. The total polarisation in a field of intensity E is then $\alpha \mathrm{E} + p$, and the work done by electric forces in bringing a molecule B into such a position is now

$$\int (\alpha \mathrm{E} + p) \,.\, \delta v_{\mathrm{B}} \,.\, d\mathrm{E} = (\tfrac{1}{2}\alpha \mathrm{E}^2 + p \,.\, \mathrm{E})\delta v_{\mathrm{B}}$$

A similar expression applies to molecules A, so that the work of adsorption is

$$w = \{\tfrac{1}{2}(\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}}) \,.\, \mathrm{E}^2 + (p_{\mathrm{A}} - p_{\mathrm{B}})\mathrm{E}\}\delta v_{\mathrm{B}}. \qquad (10)$$

so that, as in (8) and (9)

$$\Gamma = \Gamma_0 \, e^{-(a\mathrm{V}^2 + b\mathrm{V})} \qquad (11)$$

and

$$\Delta\gamma = \Delta\gamma_0 \,.\, e^{-(a\mathrm{V}^2 + b\mathrm{V})} \qquad (12)$$

where $a$ has the same value as before and

$$b = (p_{\mathrm{A}} - p_{\mathrm{B}})\, \kappa \delta v_{\mathrm{B}}/k\mathrm{T} \qquad (12\mathrm{A})$$

Writing (12) in the form

$$\begin{aligned} \Delta\gamma &= \Delta\gamma_0 \,.\, e^{-a(\mathrm{V} + b/2a)^2 + b^2/4a} \\ &= \Delta\gamma_0 \,.\, e^{b^2/4a} \,.\, e^{-a(\mathrm{V}')^2} \qquad (13) \end{aligned}$$

where $\mathrm{V}' = \mathrm{V} + b/2a$, we see that (12) gives a curve of the same shape as (9), but its maximum occurs at $\mathrm{V}_m = -b/2a$ and has the value $\Delta\gamma_m = \Delta\gamma_0 \,.\, e^{b^2/4a}$. We may therefore write (13) in the form

$$\Delta\gamma = \Delta\gamma_m \,.\, e^{-a(\mathrm{V} - \mathrm{V}_m)^2} \qquad (13\mathrm{A})$$

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* Smith, 'Phil. Trans.,' A, vol. 193, p. 48 (1899); Gouy, *loc. cit.*

The significance of these equations can easily be seen if we consider a dipole of the solute, orientated at the interface (fig. 2).

The effect of the polarity *induced by the electric field* is to attract molecules of both solute and solvent. Since the solvent molecules are attracted to a greater extent than the solute molecules, the latter are in effect repulsed, or "squeezed out" from the surface. Suppose that the dipole has its positive end orientated towards the interface. Then a negative charge on the adjacent surface will tend to attract the dipole, an effect opposite to that of the induced polarity. A positive charge will tend to repel it and will supplement the effect of the induced polarity. Now the effect of the electric field on the dipole is directly proportional to the field strength E, that of the induced polarity to $E^2$, so that with small negative charges the "dipole" effect may counterbalance the "induced" effect and the adsorption increase as the field increases. The "induced" effect increases more rapidly than the other and ultimately becomes the greater. The maximum of adsorption therefore occurs at the point at which the effect of the attraction of the dipoles is just balanced by the repulsion effect of the induced polarity.

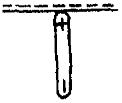

FIG. 2.

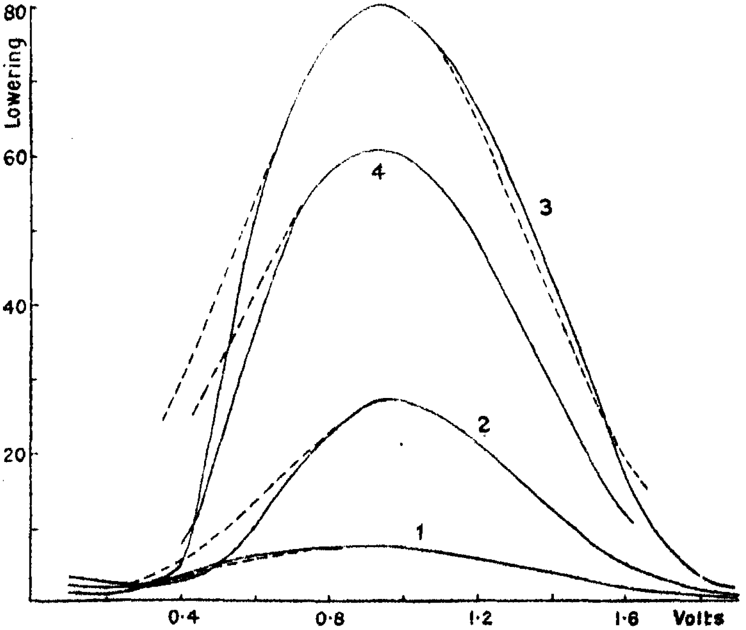

FIG. 3.—Adsorption Curves of :—

1, Methyl Alcohol (M/1).
2, Ethyl Alcohol (M/1).
3, *n*-Propyl Alcohol (M/1).
4, Allyl Alcohol (M/1).

Equation (13) is, with one or two exceptions, in fair agreement with all the curves obtained by Gouy. Figs. 3 to 5 give some examples of the agreement

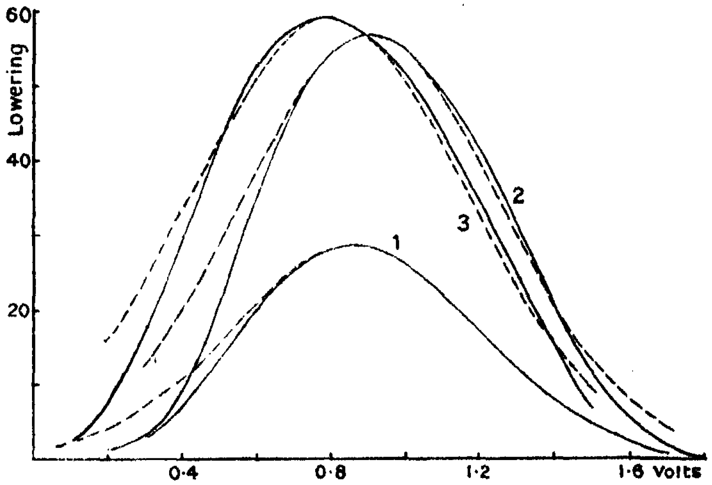

Fig. 4.—Adsorption Cuves of :—

1, Acetic Acid (M/1). 2, Propionic Acid (M/1). 3, Monochloracetic Acid (M/1).

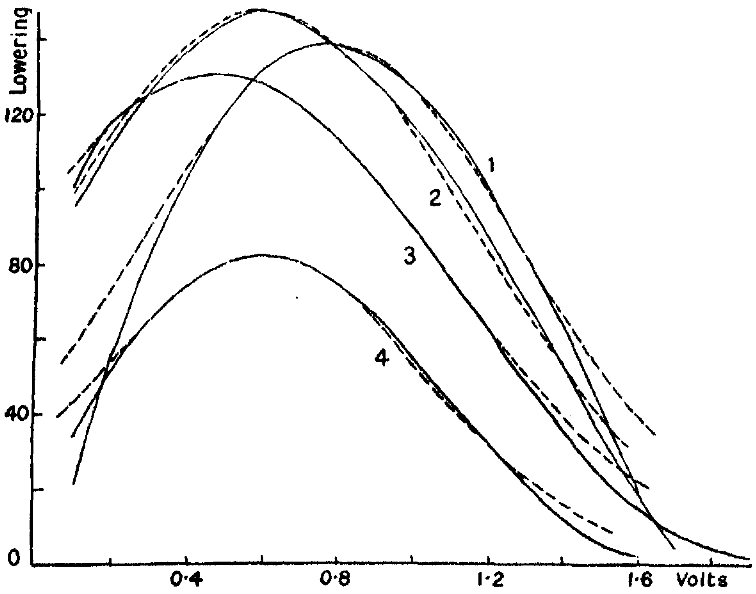

Fig. 5.—Adsorption Curves of :—

1, *o*-Cresol. 2, Orcinol. 3, Pyrogallol. 4, Hydroquinone.

of observed and calculated curves, taken from compounds of various types. The constants employed are listed in Table I and are discussed in a later section. It is to be noted that the curves in which the depression of the surface tension is still appreciable at one end are of the same type as the others. They are merely extreme cases of the displacement of the maximum.

### *Adsorption of Organic Ions.*

With the salts of the substituted ammonium derivatives we find adsorption curves having maxima at or near the extreme right (negative) end of the curve (fig. 6). Since these substances are strong electrolytes, we may consider the behaviour at the interface of organic ions.

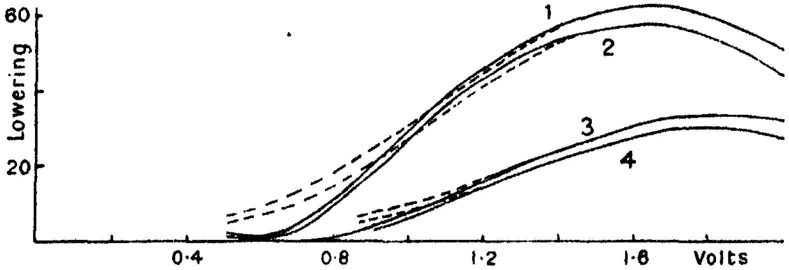

FIG. 6.—Adsorption Curves of :—

1, $N(C_2H_5)_4OH$ (M/10).
2, $N(C_2H_5)_4OH \cdot \frac{1}{2}H_2SO_4$ (M/10).
3, $N(CH_3)_4OH$ (M/10).
4, $N(CH_3)_4OH \cdot \frac{1}{2}H_2SO_4$ (M/10).

The work done in bringing up a body carrying a charge $q$ though a potential difference V is $q$V, and this term must be added to (10) in order to obtain the work done in adsorption. The form of equation (11) is not thereby affected, but $b$ is increased by the amount $q/k$T. The adsorption of a polarisable ion is thus to be regarded as an extreme case of that of a dipole.

With positive ions we get a large displacement of the maximum of adsorption to the right (negative) side. Thus the strong bases, tetramethylammonium hydroxide and tetraethylammonium hydroxide and their salts give curves having maxima at the extreme right (fig. 6). Weak bases such as triethylamine and pyridine, which are only ionised to a minute extent, themselves give normal curves, but their salts, which behave as strong electrolytes, show maxima displaced to the negative side (fig. 7). The salts of weaker bases such as d-isoamylamine, heptylamine give curves with maxima only slightly displaced to the right (1·0–1·4); presumably they are largely hydrolysed in solution.

It is unfortunate that no curves of substances giving negative organic ions have been determined.* These may be expected to give maxima considerably

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* Gouy determined the curves of salts of a few capillary inactive acids such as oxalic and tartaric. These are only slightly adsorbed.

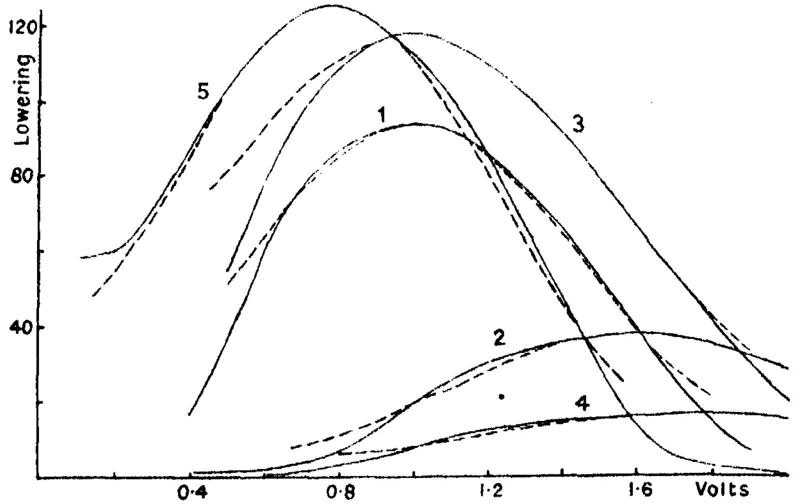

FIG. 7.—Adsorption Curves of :— (M/10).

1, Triethylamine (M/10). 3, Isobutylamine (M/1).
2, Triethylamine Sulphate (M/10). 4, Isobutylamine Sulphate (M/1).
5, Pyrrhol (sat.).

displaced to the left (positive) side. It is noteworthy that the curve of chloracetic acid which ionises to an appreciable extent, is displaced to the left of the non-substituted acids of its class.

### *Asymmetry of Positive and Negative Branches.*

A very general feature of the curves is that while the right-hand (negative) branch is very closely in accordance with the calculated values, the depression of the surface tension in the left-hand branch frequently decreases more rapidly than is required by the equations. This is illustrated in a number of cases by fig. 8, in which the logarithm of the depression is plotted against $(V - V_m)^2$, $V_m$ being the potential difference at the maximum of the curve. Equation (13A) requires a linear relation between these two quantities, but while the right-hand branch is in excellent agreement with this requirement, the points of the left-hand branch fall below.*

In making the calculation we have assumed that the electric field acting on a molecule is uniform. Actually this is not the case. The parts of an adsorbed molecule nearest the surface are probably in a more intense field than those at a greater distance. The polarisation produced in molecules by

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* The left-hand branch is sometimes also nearly linear, indicating a definite lower value of the constant on the positive side (ethyl alcohol, saccharose).

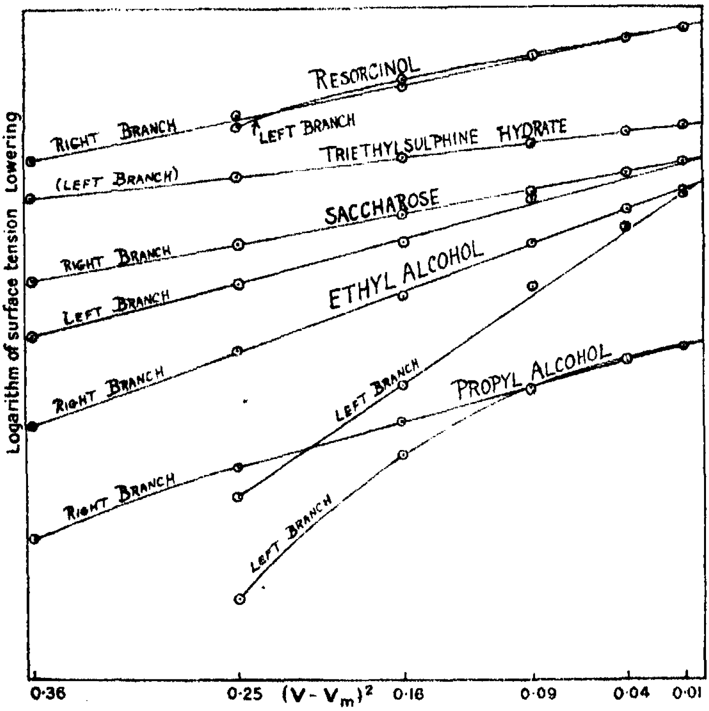

Fig. 8.—Logarithm of Surface Tension Lowering plotted against $(V - V_m)^2$.

an electric field is not uniformly distributed. Thus it is probable that in an alcohol, for example, the hydroxyl group is more polarisable than the hydrocarbon chain and the force on a molecule will depend on whether the hydroxyl group is directed towards the surface, or away from it. Since the hydroxyl group is also associated with a dipole, a reversal of the charge may reverse the direction of the molecule. In the case shown in fig. 9, the attraction on the molecule and the amount adsorbed would be greater on the negative than on the positive side. Moreover the hydroxyl group is comparable in size with the molecules of water. In case (*a*) the active part of the molecule, the hydroxyl group, is at the same distance from the interface as the water molecules and we get normal behaviour; in case (*b*) they are at a greater distance and the amount adsorbed is less than that required by the equation.

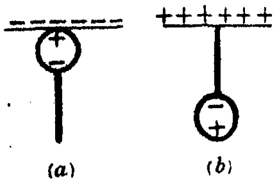

Fig. 9.

The effect is more marked in the aliphatic than in the aromatic series and we find, as we should expect, that it is generally greater the longer the chain of carbon atoms in the compound.

### *Values of the Constants.*

(1) *Values of* a.—The values of $a$ which give the best agreement with the curves determined by Gouy have been calculated in a large number of cases and are given in Tables I and II.

The electrocapillary curves of the substances in Table I were obtained in every case by adding them to the primitive solution of $Na_2SO_4$ (M/2) at the concentration shown. The values obtained are thus strictly comparable with each other. In the case of the organic bases and salts of Table II, which are sufficiently conducting in solution to permit a determination of their electrocapillary curves, Gouy usually measured a solution of the substance itself without any addition of sodium sulphate. The surface tension lowerings of these solutions have been calculated by comparison with a sodium sulphate solution of the same equivalent concentration, except in a few cases where a large excess of sulphuric acid is present and in which a solution of the latter of the same total strength is employed. On this account the values of $a$ in Table II are not strictly comparable with those in Table I and must be regarded as provisional.

Owing to the deviation of the left-hand branches from the theoretical equation, these values are obtained from the right-hand branches of the curves (except in the case of the organic bases which have only a left branch).

It is necessary to see how far we can account for these values. According to (9A):

$$a = \tfrac{1}{2}(\alpha_A - \alpha_B) \,.\, \kappa^2 \,.\, \delta v_B/k\mathrm{T} = \tfrac{1}{2}(\alpha_A - \alpha_B) \,.\, \kappa^2 \,.\, \Delta v_B/\mathrm{RT} \qquad (14)$$

where $\Delta v_B$ is the volume of the gram-molecule of the substance and R the gas constant per mol. In order to evaluate $\kappa$ in $E = \kappa V$, we have $E = 4\pi q/D$ where $q$ is the charge density at the mercury surface and D, the dielectric constant of the medium in the interface. The value of $q$ can be obtained if the capacity (*i.e.*, charge/potential difference) of the electrical double layer at the interface is known. This has been variously estimated at 13·5,[*] 18[†] and 24[‡] microfarads per square centimetre. We will take Gouy's value of 18 microfarads/cm.$^2$ as a reasonable average, so that we have: Capacity = 18 microfarads/cm.$^2$ = $18 \times 9 \times 10^5$ e.s. units; and since the potential difference V volts = V/300 e.s. units, we have:

$$q = 18 \times 9 \times 10^5\ \mathrm{V}/300 = 5{\cdot}4 \times 10^4\ \mathrm{V}\ \text{e.s. units.}$$

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[*] Kruger and Krumreich, 'Z. Electrochem.,' vol. 19, p. 617 (1913).

[†] Gouy, 'Ann. Physique,' vol. 7, p. 129 (1917).

[‡] Stern, 'Z. Electrochem.,' vol. 30, p 508 (1924).

Table I.—Values of *a* and $V_m$.

| Substance. | Constitution. | Concentration. | *a*. | $V_m$ | $\gamma_m$ |
|---|---|---|---|---|---|
| Methyl alcohol | $CH_3OH$ | M | 2·7 | 0·90 | 7·4 |
| Ethyl alcohol | $CH_3 . CH_2OH$ | M | 4·1 | 0·96 | 27·2 |
| *n*-Propyl alcohol | $CH_3 . CH_2 . CH_2OH$ | M | 3·3 | 0·95 | 79·8 |
| *iso*-Propyl alcohol | $(CH_3)_2 . CHOH$ | M | 3·5 | 0·92 | 60·7 |
| *n*-Butyl alcohol | $CH_3 . CH_2 . CH_2 . CH_2OH$ | M/10 | 5·0 | 0·92 | 49·1 |
| *iso*-Butyl alcohol | $(CH_3)_2 . CH . CH_2OH$ | M/10 | 7·1 | 0·91 | 38·6 |
| *sec*-Butyl alcohol | $CH_3 . CH_2 . CHOH . CH_3$ | M/10 | 6·4 | 0·93 | 40·0 |
| *tert*-Butyl alcohol | $(CH_3)_3 . COH$ | M/10 | 8·6 | 0·94 | 26·6 |
| *tert*-Amyl alcohol | $(C_2H_5)(CH_3)_2 . COH$ | M/10 | 6·2 | 0·90 | 62·6 |
| Heptyl alcohol | $CH_3 . (CH_2)_5 . CH_2OH$ | *sat.* | 6·9 | 0·83 | 78·4 |
| Allyl alcohol | $CH_2 . CH . CH_2OH$ | M | 3·5 | 0·93 | 60·8 |
| Acetaldehyde | $CH_3 . COH$ | M | 8·9 | 1·1 | 35·0 |
| Propionaldehyde | $CH_3 . CH_2 . COH$ | *ca.* M | 2·1 | 0·95 | 85·0 |
| *iso*-Butyl aldehyde | $(CH_3)_2 . CH . COH$ | *sat.* | 2·7 | 0·98 | 90·2 |
| Valeric aldehyde | $CH_3 . (CH_2)_3 . COH$ | *sat.* | 3·1 | 0·96 | 79·5 |
| Acetonitrile | $CH_3 . CN$ | — | 2·2 | 1·02 | 61·0 |
| Propionitrile | $CH_3 . CH_2 . CN$ | *sat.* | 1·6 | 1·01 | 87·0 |
| Capronitrile | $C_5H_{11} . CN$ | *sat.* | 4·8 | 0·95 | 77·0 |
| Acetic acid | $CH_3 . CO_2H$ | *ca.* 2M | 4·4 | 0·86 | 28·5 |
| Propionic acid | $CH_3 . CH_2 . CO_2H$ | *ca.* M | 3·0 | 0·90 | 56·6 |
| Butyric acid | $CH_3 . CH_2 . CH_2 . CO_2H$ | *sat.* | 2·8 | 0·89 | 102·6 |
| *iso*-Valeric acid | $(CH_3)_2 . CH . CH_2 . CO_2H$ | *sat.* | 3·0 | 0·87 | 98·2 |
| Monochloracetic acid | $CH_2Cl . CO_2H$ | M | 3·6 | 0·79 | 59·1 |
| Formamide | $H . CONH_2$ | M | 2·1 | 0·83 | 10·6 |
| Acetamide | $CH_3 . CONH_2$ | M | 2·3 | 0·90 | 23·3 |
| Propionamide | $C_2H_5 . CONH_2$ | *sat.* | 0·7 | 0·95 | 73·6 |
| Butyramide | $C_3H_7 . CONH_2$ | *sat.* | 1·6 | 1·0 | 87·9 |
| Acetone | $(CH_3)_2 . CO$ | M | 3·4 | 1·07 | 47·0 |
| Methyl ethyl ketone | $(CH_3)(C_2H_5) . CO$ | M | 2·0 | 1·08 | 96·6 |
| Di-ethyl ketone | $(C_2H_5)_2 . CO$ | *sat.* | 1·6 | 1·05 | 111·0 |
| Butyrone | $(C_3H_7)_2 . CO$ | *sat.* | 2·9 | 0·98 | 87·8 |

| | | | | | |
|---|---|---|---|---|---|
| Glycerol | $C_3H_5(OH)_3$ | M | 1·6 | 0·88 | 22·3 |
| Glucose | $C_6H_{12}O_6$ | M | 2·3 | 0·82 | 36·0 |
| Lactose | $C_{12}H_{22}O_{11}$ | *sat.* | 1·2 | 0·87 | 54·0 |
| Maltose | $C_{12}H_{22}O_{11}$ | M/10 | 2·8 | 0·82 | 47·0 |
| Saccharose | $C_{12}H_{22}O_{11}$ | M | 2·1 | 0·87 | 56·1 |
| Raffinose | $C_{18}H_{32}O_{16}$ | M/10 | 2·0 | 0·90 | 53·3 |
| Phenol | $C_6H_5OH$ | M/10 | 3·2 | 0·78 | 91·3 |
| *o*-Cresol | $1 . 2, C_6H_4 . CH_3 . OH$ | *sat.* | 1·9 | 0·78 | 139·0 |
| *o*-Xylenol | $1 . 2 . 3, C_6H_3 . (CH_3)_2 . OH$ | *sat.* | 2·9 | 0·78 | 100 |
| Pyrocatechol | $1 . 2, C_6H_4(OH)_2$ | M/10 | 2·4 | 0·64 | 82·6 |
| Resorcinol | $1 . 3, C_6H_4(OH)_2$ | M/10 | 2·3 | 0·59 | 90·6 |
| Hydroquinone | $1 . 4, C_6H_4(OH)_2$ | M/10 | 2·6 | 0·60 | 82·4 |
| Orcinol | $1 . 3 . 5, C_6H_3 . CH_3 . (OH)_2$ | M | 1·6 | 0·60 | 148 |
| Pyrogallol | $1 . 2 . 3, C_6H_3(OH)_3$ | M | 1·4 | 0·48 | 131·0 |
| Benzoic acid | $C_6H_5 . CO_2H$ | M/100 | 4·0 | 0·79 | 54·2 |
| *p*-Toluic acid | $1 . 4, C_6H_4 . CH_3 . CO_2H$ | *sat.* | 8·9 | 0·75 | 41·0 |
| *p*-Oxybenzoic acid | $1 . 4, C_6H_4 . OH . CO_2H$ | *sat.* | 2·8 | 0·65 | 86·0 |
| *p*-Oxybenzoic aldehyde | $1 . 4, C_6H_4 . OH . COH$ | *sat.* | 2·3 | 0·76 | 97·2 |
| *o*-Phthalic acid | $1 . 2, C_6H_4 . (CO_2H)_2$ | M/100 | 4·5 | 0·67 | 46·0 |
| Protocatechuic acid | $1 . 2 . 4, C_6H_3 . (OH)_2 . CO_2H$ | *sat.* | 2·4 | 0·60 | 108·1 |
| Protocatechuic aldehyde | $1 . 2 . 4. C_6H_3 . (OH)_2 . COH$ | *sat.* | 2·0 | 0·75 | 116·1 |
| Gallic acid | $1 . 2 . 3 . 5, C_6H_2(OH)_3 . CO_2H$ | *sat.* | 2·0 | 0·52 | 125 |
| Benzyl alcohol | $C_6H_5 . CH_2OH$ | *sat.* | 2·0 | 0·90 | 129·6 |
| Saligenin | $1 . 2, C_6H_4 . OH . CH_2OH$ | *sat.* | 1·7 | 0·79 | 128·3 |
| Vanillic acid | $1 . 2 . 4, C_6H_3 . OH . OCH_3 . CO_2H$ | *sat.* | 2·3 | 0·69 | 99·6 |
| Vanillin | $1 . 2 . 4, C_6H_3 . OH . OCH_3 . COH$ | M/100 | 3·4 | 0·80 | 82·7 |

Table II.—Values of *a* and $V_m$. Organic Bases and their Salts.

| Substance. | Constitution. | Concentration. | *a*. | $V_m$ | $\gamma_m$ | Primitive. |
|---|---|---|---|---|---|---|
| Tetra-methylammonium hydroxide | $N(CH_3)_4OH$ | M/10 | 1·7 | 1·85 | 33·7 | $Na_2SO_4$, M/10 |
| Tetra-methylammonium sulphate | $N(CH_3)_4OH$, $\frac{1}{2}H_2SO_4$ | M/10 | 2·0 | 1·80 | 30·1 | $Na_2SO_4$, M/10 |
| Tetra-ethylammonium hydroxide | $N(C_2H_5)_4OH$ | M/10 | 1·7 | 1·65 | 63·0 | $Na_2SO_4$, M/10 |
| Tetra-ethylammonium sulphate | $N(C_2H_5)_4OH$. $\frac{1}{2}H_2SO_4$ | M/10 | 1·9 | 1·62 | 57·8 | $Na_2SO_4$, M/10 |
| Tri-ethyl sulphine hydroxide | $S(C_2H_5)_3 . OH$ | M/10 | 1·2 | 1·74 | 61·8 | $Na_2SO_4$, M/10 |
| Tri-ethyl sulphine sulphate | $S(C_2H_5)_3 . OH$, $\frac{1}{2}H_2SO_4$ | M/10 | 1·2 | 1·75 | 57·3 | $Na_2SO_4$, M/10 |
| Neurine | $N(C_2H_3)(CH_3)_3 . OH$ | M/10 | 1·6 | 1·80 | 36·5 | $Na_2SO_4$, M/10 |
| Neurine sulphate | $N(C_2H_3)(CH_3)_3 . OH$, $\frac{1}{2}H_2SO_4$ | M/10 | 1·6 | 1·80 | 33·4 | $Na_2SO_4$, M/10 |
| Choline | $N(C_2H_4OH)(CH_3)_3 . OH$ | M/10 | 1·1 | 1·85 | 41·7 | $Na_2SO_4$, M/10 |
| Choline sulphate | $N(C_2H_4OH)(CH_3)_3 . OH$, $\frac{1}{2}H_2SO_4$ | M/10 | 1·5 | 1·83 | 42·6 | $Na_2SO_4$, M/10 |
| Methylamine | $CH_3 . NH_2$ | M | 3·0 | 1·15 | 22·5 | $Na_2SO_4$, M/2 |
| Methylamine sulphate | $CH_3 . NH_2$, $\frac{1}{2}H_2SO_4$ | M | $<$ 0 | — | — | $Na_2SO_4$, M/2 |
| Tri-ethylamine | $N(C_2H_5)_3$ | M/10 | 2·4 | 1·00 | 94·4 | $Na_2SO_4$, M/20 |
| Tri-ethylamine sulphate | $N(C_2H_5)_3$, $\frac{1}{2}H_2SO_4$ | M/10 | 1·9 | 1·60 | 38·6 | $Na_2SO_4$, M/20 |
| *iso*-Butylamine | $C_4H_9 . NH_2$ | M | 1·5 | 0·99 | 118·3 | $Na_2SO_4$, M/2 |
| *iso*-Butylamine sulphate | $C_4H_9 . NH_2$, $\frac{1}{2}H_2SO_4$ | M/10 | 0·9 | 1·8 | 17·2 | $Na_2SO_4$, M/20 |
| *iso*-Amylamine | $C_5H_{11} . NH_2$ | M/10 | 2·8 | 1·00 | 77·0 | $Na_2SO_4$, M/20 |
| *iso*-Amylamine sulphate | $C_5H_{11} . NH_2$ ,$\frac{1}{2}H_2SO_4$ | M/10 | 2·4 | 1·45 | 24·2 | $Na_2SO_4$, M/20 |
| Di-*iso*-amylamine sulphate | $(C_5H_{11})_2NH$, $\frac{1}{2}H_2SO_4$ | M/10 | 1·1 | 1·1 | 82·1 | $Na_2SO_4$, M/20 |
| Allylamine | $C_3H_5 . NH_2$ | M | 2·1 | 1·04 | 82·2 | $Na_2SO_4$, M/2 |
| Allylamine sulphate | $C_3H_5 . NH_2$, $\frac{1}{2}H_2SO_4$ | M | ? | 1·25 | — | $Na_2SO_4$, M/2 |
| Caffeine | $C_8H_{10}N_4O_2$ | M/100 | 2·2 | 0·93 | 84·6 | $Na_2SO_4$, M/2 |
| Caffeine sulphate | $C_8H_{10}N_4O_2$, $\frac{1}{2}H_2SO_4$ | M/100 | ? | 1·05 | — | $H_2SO_4$, M/2 |
| Aniline | $C_6H_5 , NH_2$ | M/10 | 2·3 | 0·87 | 109·6 | $Na_2SO_4$, M/2 |
| *m*-Toluidine | 1 . 3, $C_6H_5 . CH_3 . NH_2$ | *sat.* | 1·9 | 0·84 | 136·0 | $Na_2SO_4$, M/2 |
| *p*-Toluidine | 1 . 4, $C_6H_5 . CH_3 . NH_2$ | *sat.* | 1·1 | 0·88 | 96·4 | $Na_2SO_4$, M/2 |
| *p*-Toluidine sulphate | 1 . 4, $C_6H_5 . CH_2 . NH_2$, $\frac{1}{2}H_2SO_4$ | M/100 | 1·0 | 1·20 | 10·2 | $H_2SO_4$, M/2 |
| Benzylamine | $C_6H_5 . CH_2NH_2$ | *sat.* | 1·2 | 0·96 | 156·0 | $Na_2SO_4$, M/2 |
| Benzylamine sulphate | $C_6H_5 . CH_2NH_2$, $\frac{1}{2}H_2SO_4$ | M/10 | 1·1 | 1·10 | 41·4 | $Na_2SO_4$, M/2 |
| Pyrrhole | $C_4H_5N$ | *sat.* | 2·5 | 0·77 | 126·0 | $Na_2SO_4$, M/2 |
| Pyridine | $C_5H_5N$ | M/10 | 2·4 | 1·09 | 55·6 | $Na_2SO_4$, M/2 |
| Pyridine sulphate | $C_5H_5N$, $\frac{1}{2}H_2SO_4$ | M/10 | 1·0 | 1·6 | 22·7 | $Na_2SO_4$, M/2 |

Now since the liquid in the immediate vicinity of the mercury probably contains a large excess of alcohol molecules, we may put as a rough approximation $D = 31$, the dielectric constant of the alcohol so that

$$E = 4\pi \,.\, 5 \cdot 4 \times 10^4 \, V/31 = 2 \cdot 19 \times 10^4 \, V \text{ e.s. units}$$

and $\kappa = 2 \cdot 19 \times 10^4$.

Now, since the polarisation produced by an electric field in unit volume of a given substance is related to its dielectric constant by the relation,

$$P = (D - 1) \,.\, E/4\pi \,;$$

we have

$$\alpha_A = (D_A - 1)/4\pi, \qquad \alpha_B = (D_B - 1)/4\pi.$$

Thus in the case of methyl alcohol and water, $D_A = 80$, $D_B = 31$, $\Delta v_B = 40$, and $R = 1 \cdot 99 \times 4 \cdot 182 \times 10^7$ ergs., so that we find $a = 1 \cdot 55$. This is in reasonable agreement with the observed value, $a = 2 \cdot 67$, considering the uncertainty of many of the quantities entering into the calculation. Thus the value of the capacity of the electrical double layer may be in error by 50 per cent.; owing to electric saturation in the intense electric fields at the interface, the effective dielectric constant of substances there may be lower than under normal conditions; and further the proper value for the "dielectric constant" assigned to methyl alcohol molecules in aqueous solution may differ appreciably from that in the pure liquid.

In going through the homologous series of alcohols, etc., the dielectric constants do not vary greatly, so that the value of $a$ should depend chiefly on the molar volume, $\Delta v_B$ in (14), and should increase by approximately 45 per cent. of the value for methyl alcohol or 1·3 for each additional carbon atom. We find that ethyl alcohol ($a = 4 \cdot 1$) is in approximate agreement with this, but at N-propyl alcohol, $a$ drops to 3·3 and thereafter increases up the series of normal alcohols (Table III). So far as the available data goes, it appears that similar behaviour is exhibited in the series of aldehydes, nitriles, amides

Table III.—Values of $a$ of Aliphatic Alcohols.

| — | Normal. | Iso. | Secondary. | Tertiary. |
|---|---|---|---|---|
| **Methyl** | 2·7 | — | — | — |
| **Ethyl** | 4·1 | — | — | — |
| **Propyl** | 3·3 | 3·5 | — | — |
| **Butyl** | 5·0 | 7·1 | 6·4 | 8·6 |
| **Amyl** | — | — | — | 6·2 |
| **Heptyl** | 6·9 | — | — | — |

and acids. Moreover the isomers of a compound usually have a greater value of $a$ than the normal straight-chain form.

This behaviour is accounted for if we consider that molecules of methyl alcohol, comparable in size with those of water, come entirely within the range of the electric forces at the interface and have a value of $a$ which agrees with that calculated. The molecules of its homologues having long chains come only partly in the region of the electric field and are attracted less than corresponds to their volume, and so have values of $a$ less than the calculated. The isomers with branched chains are more compact and do not project so far from the interface as their long-chain prototypes. Hence they come more under the influence of the electric field and have greater values of $a$.

(2) *Values of* $V_m$.—According to (13) the value of $b$ is given by $b = -2aV_m$. Since the point of zero potential difference is unknown, we cannot determine the absolute values of $V_m$. The maxima of many curves (*e.g.*, those of the alcohols) occur within a small range and a small error in the position of the absolute zero would have a considerable effect on the values of $b$ and probably obscure the real nature of their variations. We have therefore only tabulated in Table I and II the values of $V_m$ on the standard employed by Gouy.*

Some interesting regularities are exhibited by these values. The aliphatic alcohols and acids and the carbohydrates, with one or two exceptions, have maxima between 0·8 and 0·95 volts. The curves of the aldehydes, amides, nitriles, ketones, etc., are displaced further to the right and have maxima between 0·95 and 1·1 volts. In the aromatic hydroxy-compounds the position of the maximum appears to depend chiefly on the number of phenolic hydroxy groups. Phenol and its homologues have maxima at 0·78 volts; the dihydroxy-phenols between 0·60 and 0·65 volts and trihydroxy-compounds at about 0·5. Each increase in the number of hydroxyl groups causes a definite shift to the left. The carboxylic group has nearly the same effect as the hydroxyl group, but the aldehyde radicle, —COH, causes a displacement in the opposite direction.

The dihydroxy-phenols present a point of some interest. In (12A), $p_B \delta v_B$, the permanent polarisation of a molecule B at the interface in the absence of an electric field, is equal to its electric moment, $\mu_B$, under these conditions. The value of $b$ and the position of the maximum is thus determined by $\mu_B$.

The electric moments of di-substituted benzene derivatives in a constraintless state in solution have been determined and are in accordance with a geometrical disposition of the substituent dipoles directed away from the centre of the benzene ring. Thus according to C. P. Smyth and S. O. Morgan[*] the electric moments of the dichlorobenzenes in benzene solution were :—

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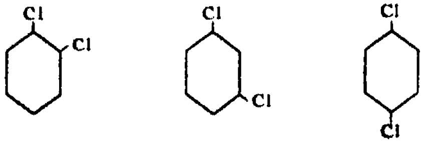
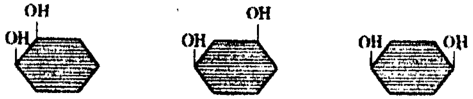
* Gouy's standard electrode consisted of mercury in a solution of sodium sulphate (M/2), saturated with mercurous sulphate.



$\mu \times 10^8$ 2·30 1·55 0

If the dihydroxy-compounds had at the interface moments related in the same way they would give widely different maxima. The fact that the latter are almost identical indicates that at the interface the hydroxyl groups are directed in the same sense in the three cases, a condition most easily brought about if they project at right angles to the plane of the benzene ring :—



A knowledge of the true values of $b$ would probably give much information as to the disposition of molecules at the interface.

### *Adsorption of more Polarisable Substances than Water.*

So far we have been considering the behaviour of substances which are less polarisable and which have a lower value of $\alpha$ (9A) than water. Water is a highly polar substance and the vast majority of organic compounds have lower dielectric constants, but we may consider, for completeness, the behaviour of a more polarisable substance for which $\alpha_B$ is greater than $\alpha_A$. Then the adsorption equation becomes

$$\Delta\gamma = \Delta\gamma_0 \, e^{a'V^2}$$

where $a'$ is a positive quantity. The substance will be adsorbed to a greater extent and the surface tension lowering increase, as the electric field increases in either direction.

No curves have been obtained which certainly exhibit this behaviour. Glycocol and certain other amino-acids, substances of a highly polar nature, cause a lowering of the surface tension which increases towards the two extremities. But the lowering produced is very small, not much greater than the experimental error, so that they cannot definitely be claimed as examples of this behaviour. Hydrocyanic acid, having a known dielectric constant greater than that of water, appeared to be a favourable case for investigation, and measurements have been made of its electrocapillary curves in sodium sulphate solutions. But it has been found to be almost inactive, causing only a slight modification of the curve of the primitive solution.

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[*] 'J. Amer. Chem. Soc.,' vol. 49, p. 1030 (1927).

### *Summary.*

The variation of the amount of a substance adsorbed from solution with the potential difference at the interface is given by the expression :

$$\Gamma = \Gamma_0 e^{-aV^2 + bV}$$

The variation with the potential difference of the surface tension lowering produced by organic substances at a mercury-aqueous solution interface is in accordance with this expression in a large number of cases. The values of the constants *a* and *b*, which have been calculated for numerous compounds, are discussed and the main features of the electrocapillary curves of solutions containing organic substances, determined by Gouy, are interpreted.

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## *On the Analysis of the First Spark Spectrum of Sulphur.*

By D. K. BHATTACHARYYA, M.Sc., Assistant Professor of Physics, Science College, Patna.

(Communicated by M. N. Saha, F.R.S.—Received October 16, 1928.)

The spark spectrum of sulphur was measured quite thoroughly by Eder and Valenta[*] in the region λ 3028·32 to λ 5819·54 in the year 1904 ; they gave wave-lengths up to the third place of decimals. In 1907, Sir Norman Lockyer[†] showed that some of the stronger lines of $S^+$ occur in the spectrum of Rigel (β-Orionis, class B8), but not in the spectra of either α-Cygni (Giant Ao) or Sirius (Dwarf Ao). After this time, no experimental or theoretical work seems to have been undertaken to elucidate the structure of this spectrum. In 1924, Millikan and Bowen[‡] published their data on the vacuum spark spectrum of sulphur within the region λ 370·2 to λ 1259·3, but the wave-lengths do not seem to have been very accurately given. A first glance at the published data showed that lines of S, $S^+$, $S^{++}$ and possibly also of higher stages have been all mixed up in these data. Hence an attempt was first made to locate certain groups. Taking the structure diagram as given by Saha, the possible transitions can be graphically located as follows :—

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[*] 'Beitrage zur Photochemie und Spectralanalyse,' p. 282, Vienna, 1904.

[†] 'Roy. Soc. Proc.,' vol. 80, p. 50 (1908).

[‡] 'Phys. Rev.,' vol. 23, p. 19 (1924).

$$\begin{tikzcd}
2K\,.\,8L & M_1 & \underset{3}{M_2} \arrow[r] \arrow[d] & M_3 \arrow[d] & & \\
& & N_1 \arrow[r] & N_2 \arrow[r] \arrow[d] & N_3 \arrow[d] & \\
& & & O_1 \arrow[r] & O_2 \arrow[d] & O_3 \\
& & & & P_1 & P_2.
\end{tikzcd}$$

The lines

$$\begin{tikzcd}
& 2M_2M_3 \arrow[dl] \\
3M_2 & \\
& 2M_2N_1 \arrow[ul]
\end{tikzcd}$$

lie in the Schumann region. An attempt to identify these lines with Millikan and Bowen's data yielded no satisfactory result. The next groups of lines are from transitions,

$$\begin{tikzcd}
2M_2N_1 & \\
& 2M_2N_2. \arrow[ul] \arrow[dl] \\
2M_2M_3 &
\end{tikzcd}$$

The group $2M_2N_1 \leftarrow 2M_2N_2$ will follow the arithmetic progression law, and hence from a knowledge of the spectra of P and $Cl^{++}$ that of $S^+$ can easily be extrapolated. The spectrum of $Cl^{++}$ has recently been partially analysed by Bowen,* but that of P is not yet elucidated. Hence the method of horizontal comparison, recently described by Messrs. Saha and Majumdar,† was next tried. A brief description of the method is given below :—

Let us compare the spectra of elements given in the table below.

Table I.

| B | C | N | O | F | Ne | Na |
|---|---|---|---|---|---|---|
| $C^+$ | $N^+$ | $O^+$ | $F^+$ | $Ne^+$ | $Na^+$ | $Mg^+$ |
| $N^{++}$ | $O^{++}$ | $F^{++}$ | $Ne^{++}$ | $Na^{++}$ | $Mg^{++}$ | $Al^{++}$ |
| $O^{+++}$ | $F^{+++}$ | $Ne^{+++}$ | $Na^{+++}$ | $Mg^{+++}$ | $Al^{+++}$ | $Si^{+++}$ |

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* 'Phys. Rev.,' vol. 31, p. 35 (1928).

† 'Indian Journal of Physics, vol. 3, p. 67 (1928).

Elements in the same vertical column of Table I have the same electronic configuration. Their spêctra follow the arithmetic progression law. Elements in the same horizontal row form a series in which the number of electrons in the $L_2$-place increases from 1 to 6 in the sixth column, and in the seventh column there is a further electron at $N_1$. If we consider the transition $xL_2M_1 \leftarrow xL_2M_2$, $x$ varying from 0 in the first column to 6 in the seventh column,

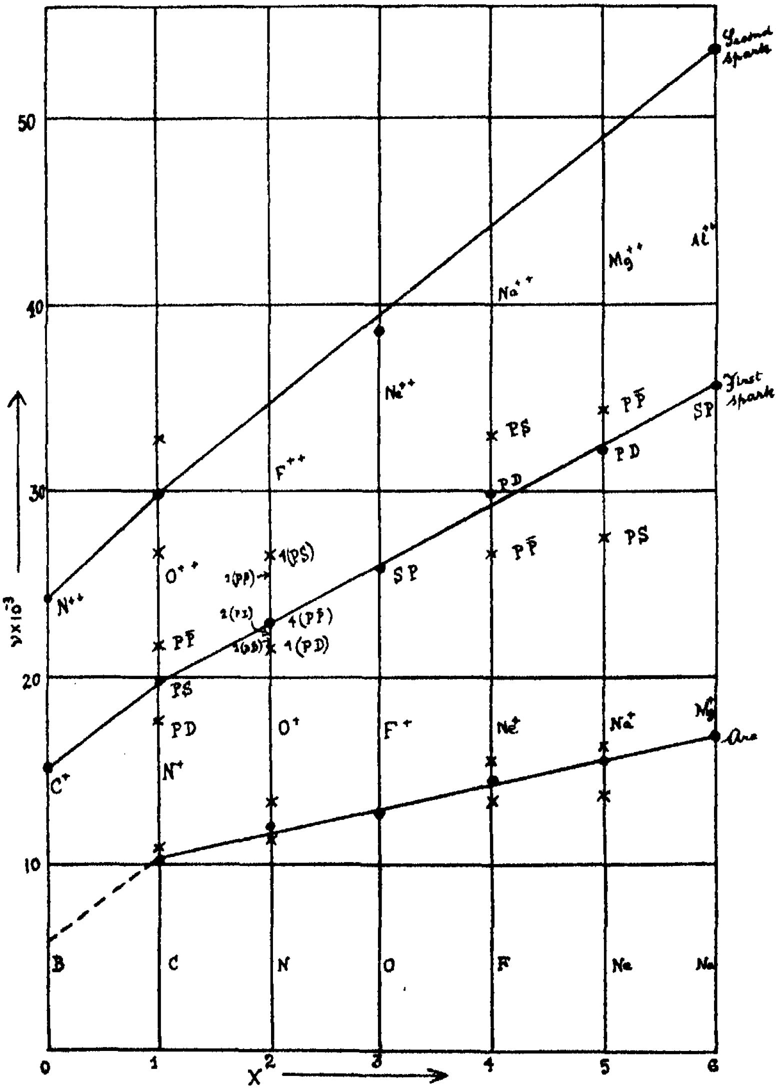

FIG. 1.

the whole set of lines may be considered as forming a group. Table II summarises our knowledge of these groups.

Table II.—$xL_2\,(M_1 \longleftarrow M_2)$.*

| Type of spectra. | $x = 0$. | $x = 1$. | $x = 2$. | $x = 3$. | $x = 4$. | $x = 5$. | $x = 6$. |
|---|---|---|---|---|---|---|---|
| Most prominent line or lines of the group | $^2S_1-{}^2P_1$ | $^3P_2-{}^3D_3$<br>$^3P_2-{}^3S_1$<br>$^3P_2-{}^3\overline{P}_2$ | $^4P_2-{}^4D_2$<br>$^4P_3-{}^4P_2$<br>$^4P_2-{}^4S_2$ | $^5S_2-{}^5P_3$ | $^4P_3-{}^4\overline{P}_2$<br>$^4P_3-{}^4D_4$<br>$^4P_3-{}^4S_2$ | $^3P_1-{}^3S_1$<br>$^3P_2-{}^3D_3$<br>$^3P_1-{}^3\overline{P}_2$ | $^2S_1-{}^2P_2$ |
|  | B | C | N | O | F | Ne | Na |
| Arc |  | 10348<br>10993 | 11475<br>12175<br>13433 | 12860 | 13360<br>14582<br>15747 | 13798<br>15615<br>16399 | 16973 |
|  | C+ | N+ | O+ | F+ | Ne+ | Na+ | Mg+ |
| First spark | 15198 | 17602<br>19816<br>21590 | 21446<br>23052<br>26821 | 25967 | 26767<br>29977<br>33004 | 27530<br>32320<br>34411 | 35761 |
|  | N++ | O++ | F++ | Ne++ | Na++ | Mg++ | Al++ |
| Second spark | 24399 | 26589<br>29925<br>32808 |  | 38545 |  |  | 53918 |

Messrs. Saha and Majumdar have shown that if the lines corresponding to elements in any one horizontal row are plotted on a graph paper, then the principal groups lie on a straight line. Fig. 1 reproduced from their paper illustrates this point clearly. In the case before us, we have to consider the spectra of the following groups :—

Table III.

| Al | Si | P | S | Cl | A | K |
|---|---|---|---|---|---|---|
| Si+ | P+ | S+ | Cl+ | A+ | K+ | Ca+ |
| P++ | S++ | Cl++ | A++ | K++ | Ca++ | Sc++ |
| S+++ | Cl+++ | A+++ | K+++ | Ca+++ | Sc+++ | Ti+++ |

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* References to the sources from which these data have been taken will be found in the paper of Saha and Majumdar, *loc. cit.*

Table IV.—$xM_2$ $(N_1 \leftarrow N_2)$.

| Type of spectra. | $x = 0$. | $x = 1$. | $x = 2$. | $x = 3$. | $x = 4$. | $x = 5$. | $x = 6$. |
|---|---|---|---|---|---|---|---|
| Most prominent line or lines of the group | ${}^2S_1-{}^2P_2$ | ${}^3P_2-{}^3D_3$<br>${}^3P_2-{}^3S_1$<br>${}^3P_2-{}^3P_2$ | ${}^4P_2-{}^4D_2$<br>${}^4P_2-{}^4P_2$<br>${}^4P_2-{}^4S_2$ | ${}^5S_2-{}^5P_3$ | ${}^4P_2-{}^4\bar{P}_2$<br>${}^4P_3-{}^4D_4$<br>${}^4P_2-{}^4S_2$ | ${}^3P_1-{}^3S_1$,<br>${}^3P_2-{}^3D_3$<br>${}^3P_1-{}^3P_2$ | ${}^2S_1-{}^2P_2$ |
| | **Al** | Si | P | S | Cl | A | L |
| Arc | 7617 | (8902)<br>(9650) | (10910) | 11044 | | 10351<br>12318<br>13380 | 13043 |
| | Si$^+$ | P$^+$ | S$^+$ | Cl$^+$ | A$^+$ | K$^+$ | Ca$^+$ |
| First spark | 15751 | 16453<br>18877<br>18425 | *18330*<br>*19864*<br>*20762* | 20784 | 25962·6 | 20701<br>23881<br>24917 | 25414 |
| | P$^{++}$ | S$^{++}$ | Cl$^{++}$ | A$^{++}$ | K$^{++}$ | Ca$^{++}$ | Sc$^{++}$ |
| Second spark | 23678 | | 27238<br>30030<br>31845 | | | 28258<br>34475<br>35811 | 37039 |

Fig. 2 represents clearly the application of the irregular doublet law, as well as that of the method of horizontal comparison applied to elements in Table III. In this case, also, it is seen that both laws are very well obeyed. We can easily locate the lines $xM_2$ $(N_1 \leftarrow N_2)$ and $xM_2$ $(N_2 \leftarrow N_3)$ with the aid of these two methods. But a very important group of lines belonging to the elements given in Table III, viz., those arising from the transition $xM_2(N_2 \leftarrow M_3)$ remains outside the range of application of both the laws. These transitions are not, as far as is known, amenable to any laws. A glance at fig. 2 shows that the principal groups of visible lines of S$^+$, due to the transition $2M_2(N_1 \leftarrow N_2)$, can be approximately located, thus :—

${}^4P - {}^4D$ at 18,000
${}^4P - {}^4\bar{P}$ at 20,000
${}^4P - {}^4S$ at 21,000.

A careful perusal of Eder and Valenta's table of lines shows that there are strong groups of lines in these regions. Further clue was afforded from Keeler's* identification that the S$^+$-lines λ 5504 and λ 5032 alone occur in the spectrum of Rigel. These two lines are described by him as being very weak in the spectrogram of Rigel. These two lines must therefore be identified

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* Lockyer, *loc. cit.*, p. 53.

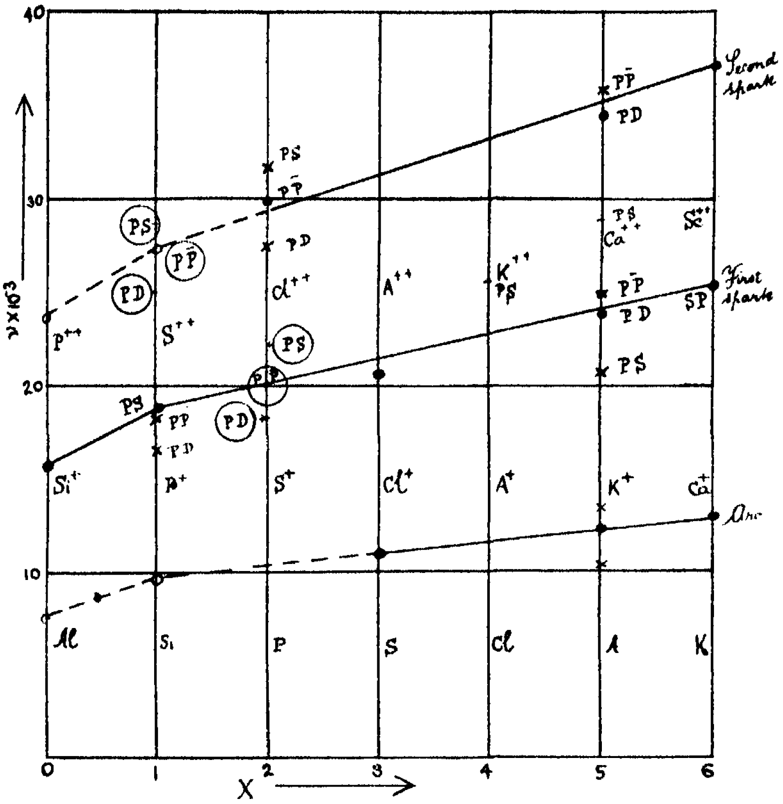

FIG. 2.—Small circles indicate the expected groups of lines of $S^+$ and $S^{++}$.

with the strongest lines ${}^4P_3 - {}^4D_4$, and ${}^4P_3 - {}^4\overline{P}_3$ respectively. With this clue for guidance the following multiplets were then easily obtained.

Table V.

| $4M_2N_2$ / $4M_3N_1$ | $c\,{}^4D_1$ | $c\,{}^4D_2$ | $c\,{}^4D_3$ | $c\,{}^4D_4$ | $c\,{}^4\overline{P}_1$ | $c\,{}^4\overline{P}_2$ | $c\,{}^4\overline{P}_3$ | $c\,{}^4S_2$ |
|---|---|---|---|---|---|---|---|---|
| $b\,{}^4P_1$ | (8)<br>18263·8 | (9)<br>18414·8 | | | (2)<br>20226·4 | (6)<br>20296·9 N | | (3)<br>21467·4 |
| $b\,{}^4P_2$ | (4)<br>17993·1 | (10)<br>18144·4 | (10)<br>18401·0 | | (6)<br>19955·6 N | (5)<br>20025·9 N | (5)<br>20301·9 N | (4)<br>21196·8 N |
| $b\,{}^4P_3$ | | (2u)<br>17707·0 | (8)<br>17964·1 | (10)<br>18330·1 K<br>(λ 5454) | | (4)<br>19588·8 | (8)<br>19864·7 K<br>(λ 5032) | (4)<br>20762·7 N |

Lines marked K were identified by Keeler in Rigel.
Lines marked N were identified by Sir Norman Lockyer in Rigel.

With the aid of the differences obtained in the group of terms arising from the $4M_2N_2$ combination, an attempt was next made to locate the lines $4M_2(N_2 \leftarrow N_3)$ and $4M_2(M_3 \leftarrow N_2)$. Here also Lockyer's observations again proved to be very useful. Lockyer had ascribed a strong group of stellar lines in the violet and blue region to $S^+$. They can arise only from one of the above transitions $4M_2(M_3 \leftarrow N_2)$ or $4M_2(N_2 \leftarrow N_3)$. These lines are reproduced from Lockyer's paper in Table VI.

Table VI.

| Eder and Valenta. Vacuum tube. | | Rigel (Kensington). | |
|---|---|---|---|
| λ. | Int. max. 10. | λ. | Int. max. 10. |
| 4142·39 | 8 | 4142·8 | 1 |
| 4145·27 | 7 | 4145·5 | 1 |
| 4153·27 | 9 | 4153·7 | 1—2 |
| 4162·86 | 10 | 4163·0 | 2—3 |
| 4174·47 | 7 | ? 4174·6 | ? 2 |
| 4253·77 | 10 } | — | — |
| 4285·13 | 8 } | | |
| 4294·56 | 8 | 4294·3 | 1 |
| 4464·62 | 5 | 4464·5 | 1 |
| 4525·16 | 6 | 4525·3 | 1—2 |
| 4552·59 | 5 | 4552·8 | 2 |
| 4716·38 | 4 | 4715·9 | 1—2 |
| 4814·97 | 4 | 4815·7 | 3 |
| 4917·41 | 4 | 4917·6 | 1 |
| 4924·27 | 5 | 4924·1 | 4 |
| 4925·49 | 6 | 4925·7 | 1 |
| 4992·15 | 5 | 4992·5 | 1 |
| 5009·76 | 6 | 5010·0 | 1—2 |
| 5014·25 | 8 | 5014·4 | 1 |
| 5027·41 | 4 | 5027·8 | 1—2 |
| 5032·66 | 8 | 5032·9 | 3 |

It appears that Lockyer's lines λ 4253·63 and λ 4285·03 must be ascribed to $S^{++}$, as they occur only in hotter stars. The other lines are due to the transitions $4M_2(N_2 \leftarrow N_3)$ as the following table shows.

Table VII.

| $4M_2N_2$<br>$4M_2N_3$ | $c\,{}^4D_1$ | $c\,{}^4D_2$ | $c\,{}^4D_3$ | $c\,{}^4D_4$ | $c\,{}^4\bar{P}_1$ | $c\,{}^4\bar{P}_2$ | $c\,{}^4\bar{P}_3$ | $c\,{}^4S_2$ |
|---|---|---|---|---|---|---|---|---|
| $d\,{}^4F_2$ | (8*ur*)<br>24133·9 N | (4)<br>23982·4 | ? | | ? | ? | ? | |
| $d\,{}^4F_3$ | | (10)<br>24117·1 N | (5)<br>23860·2 | ? | | ? | (5)<br>21959·4 N | |
| $d\,{}^4F_4$ | | | (10*ur*)<br>24070·6 N | (4)<br>23704·6 | | | ? | |
| $d\,{}^4F_5$ | | | | (10*ur*)<br>24015·2 N | | | | |
| $d\,{}^4\bar{D}_1$ | (2*u*)<br>25326·5 | (3*u*)<br>25176·6 | | | (3)<br>23365·2 | (1)<br>23294·8 | | ? |
| $d\,{}^4D_2$ | (1)<br>25374·2 | (3*u*)<br>25224·5 | (1)<br>24967·7 | | (4)<br>23413·0 | (3)<br>23343·0 | (1)<br>23067·2 | ? |
| $d\,{}^4\bar{D}_3$ | | (1*u*)<br>25303·7 | (4)<br>25048·4 | (2)<br>24682·4 | | (4)<br>23423·8 | (3)<br>23147·8 | ? |
| $d\,{}^4\bar{D}_4$ | | | (3*u*)<br>25177·8 | (6)<br>24813·1 | | | (8*u*)<br>23278·7 | |
| $d\,{}^4P_1$ | (2*u*)<br>26017·4 | (1)<br>25867·5 | | | ? | (3)<br>22984·4 | | ? |
| $d\,{}^4P_2$ | (10)<br>26044·9* | (3*u*)<br>25893·8 | (2*ur*)<br>25637·1 | | ? | (5)<br>22957·0 | ? | (2)<br>22892·4 |
| ${}^4P_3$ | | (8)<br>26048·7* | (2*u*)<br>25790·2 | (3)<br>25424·5 | | ? | ? | (1)<br>22995·0 |
| $4M_2O_1$ | | | | | | | | |
| $e\,{}^4P_1$ | (2*ur*)<br>22432·4 | (2)<br>22281·1 | | | ? | ? | | ? |
| $e\,{}^4P_2$ | ? | (3)<br>22554·0 | (4)<br>22297·0 | | (1)<br>20741·8 | ? | ? | ? |
| $e\,{}^4P_3$ | | ? | (2)<br>22762·2 | (5*ur*)<br>22396·4 | | ? | (2)<br>20860·9 | (1)<br>19966·9 |

**Lines marked N were identified by Sir Norman Lockyer in Rigel.**
*** Lines 26044·9, 26048·7 are $S^{++}$ lines. Most probably $S^{+}$ lines at these places are masked by them.**

Table VIII contains a list of all lines classified.

Table VIII.

| λ. | Int. | ν. | |
|---|---|---|---|
| 5645·92 | 2*u* | 17707·0 | $b\,{}^4\mathrm{P}_3 - c\,{}^4\mathrm{D}_2$ |
| 5565·10 | 8 | 17964·1 | $b\,{}^4\mathrm{P}_3 - c\,{}^4\mathrm{D}_3$ |
| 5556·14 | 4 | 17993·1 | $b\,{}^4\mathrm{P}_2 - c\,{}^4\mathrm{D}_1$ |
| 5509·80 | 10 | 18144·4 | $b\,{}^4\mathrm{P}_2 - c\,{}^4\mathrm{D}_2$ |
| 5473·79 | 8 | 18263·8 | $b\,{}^4\mathrm{P}_1 - e\,{}^4\mathrm{D}_1$ |
| 5454·00 | 10 | 18330·1 | $b\,{}^4\mathrm{P}_3 - c\,{}^4\mathrm{D}_4$ |
| 5432·99 | 10 | 18401·0 | $b\,{}^4\mathrm{P}_2 - c\,{}^4\mathrm{D}_3$ |
| 5428·91 | 9 | 18414·8 | $b\,{}^4\mathrm{P}_1 - c\,{}^4\mathrm{D}_2$ |
| 5103·53 | 4 | 19588·8 | $b\,{}^4\mathrm{P}_3 - c\,{}^4\bar{\mathrm{P}}_2$ |
| 5032·66 | 8 | 19864·7 | $b\,{}^4\mathrm{P}_3 - c\,{}^4\bar{\mathrm{P}}_3$ |
| 5009·76 | 6 | 19955·5 | $b\,{}^4\mathrm{P}_2 - c\,{}^4\bar{\mathrm{P}}_1$ |
| 5007·01 | 1 | 19966·4 | $c\,{}^4\mathrm{S}_2 - e\,{}^4\mathrm{P}_3$ |
| 4992·15 | 5 | 20025·9 | $b\,{}^4\mathrm{P}_2 - c\,{}^4\bar{\mathrm{P}}_2$ |
| 4942·65 | 2 | 20226·4 | $b\,{}^4\mathrm{P}_1 - c\,{}^4\bar{\mathrm{P}}_1$ |
| 4925·49 | 6 | 20296·9 | $b\,{}^4\mathrm{P}_1 - c\,{}^4\bar{\mathrm{P}}_2$ |
| 4924·27 | 5 | 20301·9 | $b\,{}^4\mathrm{P}_2 - c\,{}^4\bar{\mathrm{P}}_3$ |
| 4819·83 | 1 | 20741·8 | $c\,{}^4\bar{\mathrm{P}}_1 - e\,{}^4\mathrm{P}_2$ |
| 4815·00 | 4 | 20762·7 | $b\,{}^4\mathrm{P}_1 - c\,{}^4\mathrm{S}_2$ |
| 4792·33 | 2 | 20860·9 | $c\,{}^4\bar{\mathrm{P}}_3 - e\,{}^4\mathrm{P}_3$ |
| 4716·38 | 4 | 21196·8 | $b\,{}^4\mathrm{P}_3 - c\,{}^4\mathrm{S}_2$ |
| 4656·92 | 3 | 21467·4 | $b\,{}^4\mathrm{P}_1 - c\,\mathrm{S}_2$ |
| 4552·59 | 5 | 21959·4 | $c\,{}^4\bar{\mathrm{P}}_3 - d\,{}^4\mathrm{F}_3$ |
| 4486·86 | 2 | 22281·1 | $c\,{}^4\mathrm{D}_2 - e\,{}^4\mathrm{P}_1$ |
| 4483·65 | 4 | 22297·0 | $c\,{}^4\mathrm{D}_3 - e\,{}^4\mathrm{P}_2$ |
| 4463·76 | 5*ur* | 22396·4 | $c\,{}^4\mathrm{D}_4 - e\,{}^4\mathrm{P}_3$ |
| 4456·58 | 2*ur* | 22432·4 | $c\,{}^4\mathrm{D}_1 - e\,{}^4\mathrm{P}_1$ |
| 4432·56 | 3 | 22554·0 | $c\,{}^4\mathrm{D}_2 - e\,{}^4\mathrm{P}_2$ |
| 4392·01 | 2 | 22762·2 | $c\,{}^4\mathrm{D}_3 - e\,{}^4\mathrm{P}_3$ |
| 4333·95 | 1 | 23067·2 | $c\,{}^4\bar{\mathrm{P}}_3 - d\,{}^4\bar{\mathrm{D}}_2$ |
| 4318·85 | 3 | 23147·8 | $c\,{}^4\bar{\mathrm{P}}_3 - d\,{}^4\bar{\mathrm{D}}_3$ |
| 4294·56 | 8*u* | 23278·7 | $c\,{}^4\bar{\mathrm{P}}_3 - d\,{}^4\bar{\mathrm{D}}_4$ |
| 4291·61 | 1 | 23294·8 | $c\,{}^4\bar{\mathrm{P}}_2 - d\,{}^4\bar{\mathrm{D}}_1$ |
| 4282·74 | 3 | 23343·0 | $c\,{}^4\bar{\mathrm{P}}_2 - d\,{}^4\bar{\mathrm{D}}_2$ |
| 4278·67 | 3 | 23365·2 | $c\,{}^4\bar{\mathrm{P}}_1 - d\,{}^4\bar{\mathrm{D}}_1$ |
| 4269·94 | 4 | 23413·0 | $c\,{}^4\bar{\mathrm{P}}_1 - d\,{}^4\bar{\mathrm{D}}_2$ |
| 4267·96 | 4 | 23423·8 | $c\,{}^4\bar{\mathrm{P}}_2 - d\,{}^4\bar{\mathrm{D}}_3$ |
| 4217·40 | 4 | 23704·6 | $c\,{}^4\mathrm{D}_4 - d\,{}^4\mathrm{F}_4$ |
| 4189·90 | 5 | 23860·2 | $c\,{}^4\mathrm{D}_3 - d\,{}^4\mathrm{F}_3$ |
| 4168·55 | 4 | 23982·4 | $c\,{}^4\mathrm{D}_2 - d\,{}^4\mathrm{F}_2$ |
| 4162·86 | 10*ur* | 24015·2 | $c\,{}^4\mathrm{D}_4 - d\,{}^4\mathrm{F}_5$ |
| 4153·27 | 10*ur* | 24070·6 | $c\,{}^4\mathrm{D}_3 - d\,{}^4\mathrm{F}_4$ |
| 4145·27 | 10 | 24117·1 | $c\,{}^4\mathrm{D}_2 - d\,{}^4\mathrm{F}_3$ |
| 4142·39 | 8*ur* | 24133·9 | $c\,{}^4\mathrm{D}_1 - d\,{}^4\mathrm{F}_2$ |
| 4050·33 | 2 | 24682·4 | $c\,{}^4\mathrm{D}_4 - d\,{}^4\bar{\mathrm{D}}_3$ |
| 4028·99 | 6 | 24813·1 | $c\,{}^4\mathrm{D}_4 - d\,{}^4\bar{\mathrm{D}}_4$ |
| 4004·04 | 1 | 24967·7 | $c\,{}^4\mathrm{D}_3 - d\,{}^4\bar{\mathrm{D}}_2$ |

Table VIII—(continued).

| $\lambda$. | Int. | $\nu$. | |
|---|---|---|---|
| 3991·14 | 4 | 25048·4 | $c\,{}^4D_3 - d\,{}^4\overline{D}_3$ |
| 3970·82 | 3*u* | 25176·6 | $c\,{}^4D_2 - d\,{}^4\overline{D}_1$ |
| 3970·64 | 3*u* | 25177·8 | $c\,{}^4D_3 - d\,{}^4\overline{D}_4$ |
| 3963·28 | 3*u* | 25224·5 | $c\,{}^4D_2 - d\,{}^4\overline{D}_2$ |
| 3950·87 | 1*u* | 25303·7 | $c\,{}^4D_2 - d\,{}^4\overline{D}_3$ |
| 3947·33 | 2*u* | 25326·5 | $c\,{}^4D_1 - d\,{}^4\overline{D}_1$ |
| 3939·90 | 1 | 25374·2 | $c\,{}^4D_1 - d\,{}^4\overline{D}_2$ |
| 3932·10 | 3 | 25424·5 | $c\,{}^4D_4 - d\,{}^4P_3$ |
| 3899·50 | 2*ur* | 25637·1 | $c\,{}^4D_3 - d\,{}^4P_2$ |
| 3876·35 | 2*u* | 25790·2 | $c\,{}^4D_2 - d\,{}^4P_3$ |
| 3864·77 | 1 | 25867·5 | $c\,{}^4D_2 - d\,{}^4P_1$ |
| 3860·83 | 3*u* | 25893·8 | $c\,{}^4D_2 - d\,{}^4P_2$ |
| 3842·50 | 2*u* | 26017·4 | $c\,{}^4D_1 - d\,{}^4P_1$ |

An attempt was next made to identify the doublet spectrum of $S^+$. Owing to the intrinsic difficulty of the problem, the attempt was first directed to the discovery of the intercombination lines

$$
\begin{aligned}
{}^2P_{12}\ (\text{of } {}^4M_2N_1) - {}^4D_{1234}\ (\text{of } {}^4M_2N_2)&\\
\text{and } {}^4P_{123}\ (\text{of } {}^4M_2N_2)&\\
{}^2D_{23}\ (\text{of } {}^4M_2N_1) - {}^4D_{1234}\ (\text{of } {}^4M_2N_2)&\\
\text{and } {}^4P_{123}\ (\text{of } {}^4M_2N_2).&
\end{aligned}
$$

These lines should lie in the red and infra-red. As Eder and Valenta's data did not extend beyond λ 5819·54 on the red side, a series of experiments were undertaken for measuring the lines in this region. Great difficulty was experienced in the design of a sparking tube, and after a good deal of trial with tubes containing compounds of sulphur ($SH_2$, $SO_2$, … , etc.), a pure sulphur tube of Wood type* was designed. This tube being made of Pyrex glass could stand higher electric pressures and condensed discharges for any length of time. An induction coil of 12 inch spark provided with a mercury interrupter was run by a main supply of 110 volts D.C. A variable condenser made of thick glass (each plate being 35 cm. × 23 cm. × 4 mm.) plates and zinc sheets (each being 20 cm. × 14 cm.) immersed in kerosene oil and a variable spark-gap were used for the condensed discharge. The spark gap and the condenser plates were so altered that the banded structure of the spectrum disappeared and lines appeared in the field of view of the direct vision spectroscope.

* Wood and Kimura, 'Astrophysical Journal,' vol. 46, p. 181.

The final glow of the discharge was greenish-white. The spectrum was produced by a 2-inch concave grating of 5 feet radius, having a dispersion of 11·3 A. per millimetre. Photographs were taken on red-sensitive plates, using a malachite-green filter. Lines thus obtained are given in Table VIII. The wave-lengths are given correct to the first decimal place. Attempts are being made to extend the measurements above λ 7715·3 and below λ 3028·3.

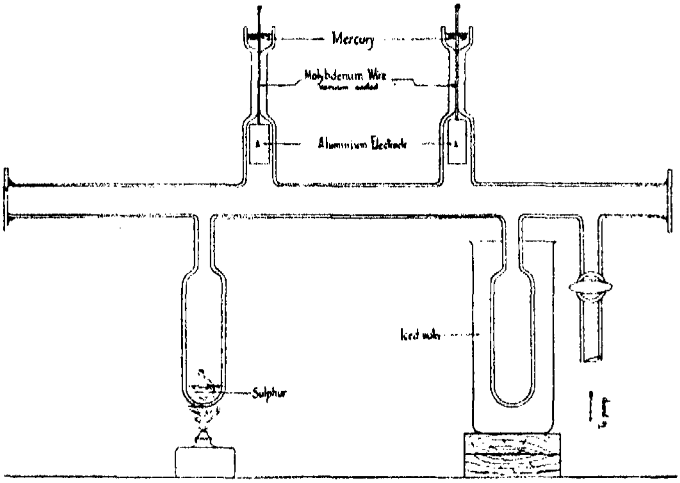

Fig. 3.

Table IX.

| $\lambda_{vac.}$ | Int. max. 10. | $\nu_{vac.}$ | $\lambda_{vac.}$ | Int. max. 10. | $\nu_{vac.}$ |
|---|---|---|---|---|---|
| 5711·8 | 5 | 17502·8 | 6347·1 | 2*u* | 15750·9 |
| 5712·3 | 4 | 17501·4 | 6357·7 | 6*u* | 15724·6 |
| 5732·2 | 0 | 17440·5 | 6359·4 | 0 | 15711·9 |
| 5748·3 | 2 | 17391·6 | 6378·6 | 8 | 15673·1 |
| 5758·5 | 1 | 17360·8 | 6381·4 | 1 | 15665·7 |
| 5928·6 | 1 | 16862·7 A ? | 6393·6 | 1 | 15636·3 |
| 5929·6 | 3 | 16860·0 | 6397·7 | 0 | 15625·8 |
| 5931·9 | 2 | 16853·2 | 6444·7 | 0 | 15512·3 |
| 5933·3 | 2 | 16849·5 | 6453·6 | 2 | 15490·9 |
| 5941·9 | 3 | 16824·9 | 6466·5 | 3 | 15460·1 |
| 5944·2 | 1 | 16818·5 | 6481·7 | 10 | 15423·8 |
| 6168·0 | 3*u* | 16208·2 | 6481·9 | 6 | 15423·1 |
| 6173·8 | 3*u* | 16193·0 S ? | 6493·5 | 0 | 15395·8 |
| 6244·2 | 3*u* | 16010·4 | 6560·9 | 3*u* | 15237·6 |
| 6245·2 | 0 | 16007·9 | 6575·4 | 1 | 15204·2 |
| 6254·7 | 0 | 15983·5 | 6577·9 | 4 | 15198·3 |
| 6283·9 | 6 | 15909·3 | 6578·9 | 3 | 15195·9 |
| 6313·3 | 0 | 15835·2 | 6582·8 | 3 | 15187·0 |
| 6327·9 | 0 | 15798·7 | 6610·4 | 5 | 15123·2 N ? |
| 6340·5 | 1 | 15767·3 | 6630·5 | 4*u* | 15077·7 |
| 6341·2 | 6*u* | 15765·5 | 6640·7 | 0 | 15054·5 |

Table IX—(continued).

| $\lambda_{\text{vac.}}$ | Int. max. 10. | $\nu_{\text{vac.}}$ | $\lambda_{\text{vac.}}$ | Int. max. 10. | $\nu_{\text{vac.}}$ |
|---|---|---|---|---|---|
| 6643·5 | 0 | 15048·2 | 7165·5 | 3 | 13952·0 |
| 6647·4 | 1 | 15039·3 | 7175·1 | 3 | 13933·4 |
| 6654·7 | 1 | 15022·8 | 7176·8 | 3*u* | 13931·0 |
| 6659·0 | 0 | 15013·1 | 7187·1 | 2*u* | 13910·0 |
| 6670·8 | 0 | 14986·6 | 7204·2 | 2 | 13877·0 |
| 6730·7 | 0 | 14853·2 | 7216·0 | 1 | 13854·0 |
| 6735·4 | 0 | 14842·8 | 7219·4 | 2*u* | 13847·8 |
| 6741·9 | 0 | 14828·5 | 7255·7 | 2 | 13777·9 |
| 6758·5 | 1 | 14792·1 S ? | 7383·7 | 0 | 13539·6 A ? |
| 6874·7 | 10 | 14542·0 | 7388·1 | 0 | 13531·7 |
| 6941·9 | 1 | 14401·2 | 7394·1 | 2 | 13520·7 |
| 6983·4 | 2 | 14315·7 | 7400·6 | 1 | 13508·5 |
| 7021·9 | 0 | 14237·4 | 7428·4 | 3 | 13458·1 |
| 7027·9 | 0 | 14225·3 | 7470·5 | 5 | 13382·3 |
| 7068·4 | 6 | 14143·5 | 7480·0 | 4*u* | 13365·3 |
| 7080·0 | 2 | 14120·4 | 7618·9 | 1*u* | 13121·8 |
| 7088·0 | 2 | 14104·5 | 7634·3 | 3*u* | 13095·2 |
| 7142·6 | 10 | 13996·8 | 7641·5 | 0*u* | 13082·9 |
| 7152·3 | 3 | 13977·1 | 7666·2 | 0 | 13040·7 |
| 7153·6 | 2 | 13975·2 | 7713·7 | 0 | 12960·4 |
| 7164·2 | 0 | 13954·0 | 7715·3 | 0 | 12957·7 |

Impurity lines of O, N, C have been looked for. Some lines of $N^+$ and $O^+$ appeared when the tube leaked a little, but, with proper precautions, these could be suppressed. A study of the sulphur spectrum in this region was previously made by Bungartz.* Excepting two lines λ 6173·8, λ 6983·4, all the above lines are different. Bungartz apparently used a lower excitation and did not get lines of $S^+$. From this list, a number of intercombinations have been discovered, but as they are not quite definite, they are not given here.

In the course of the experiments, an interesting band spectrum of sulphur in the near infra-red extending from λ 7574 to λ 7057 was discovered. The bands have a close resemblance to the A, B, $\alpha$, $\alpha'$, $\alpha''$ bands of oxygen, and will form the subject of another paper.

[*Added November* 26, 1928.—After the paper was sent to the press a paper appeared by Ingram on the classification of the lines of $S^+$. It is gratifying to note that Ingram's analysis is practically identical with that of mine so far as the quartet terms are concerned. But Ingram has gone further and has identified the fundamental lines $3M_2 \leftarrow 2M_2N_1$ with Dr. Bowen's vacuum spectrograph data. In addition, he has further identified the $^4D - {}^4F$

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* Bungartz, 'Ann. der Physik,' vol. 76, p. 720 (1925).

lines of the transition $2M_2\,(M_3 \leftarrow N_2)$ and doublet lines of $2M_2\,(N_1 \leftarrow N_2)$. The doublet group $^2P - {}^2\bar{P}$ (20500) was also identified by me by marking its position on graph No. 2 from analogy of the position of the corresponding $O^+$ group in graph No. 1. It appears that a number of intercombination lines, in addition to some more quartet-quartet and doublet-doublet combination lines of the transition $2M_2\,(M_3 \leftarrow N_2)$. can be traced in my deep-red data. They are given below :--

| | | | |
|---|---|---|---|
| 13778 .... | $c'\,^4D_4 - c\,^4D_3$ | 13954 .... | $c'\,^4F_3 - c\,^4D_2$ |
| 13848 .... | $c'\,^4D_3 - c\,^4D_2$ | 15054 .... | $b\,^2P_2 - c\,^4D_1$ |
| 13954 .... | $c'\,^4D_2 - c\,^4D_1$ | 15204 .... | $b\,^2P_2 - c\,^4D_2$ |
| 14104 .... | $c'\,^4D_2 - c\,^4D_2$ | 15460 .... | $b\,^2P_2 - c\,^4D_3$ |
| 14104 .... | $c'\,^4D_3 - c\,^4D_3$ | 15724 .... | $b\,^2P_1 - c\,^4D_2$ |
| 14143 .... | $c'\,^4D_4 - c\,^4D_4$ | 16381 .... | $c'\,^2F_3 - c\,^2D_3$ |
| 15835 .... | $c'\,^2F_3 - c\,^2D_2$ | | |
| 15909 .... | $c'\,^2F_4 - c\,^2D_3$* | | |

If this identification be correct the value of the doublet terms of Ingram will have to be raised by about 1000 units. The fundamental terms of the spectrum of $S^{++}$ are $^3P$, $^1\bar{D}_2$, $^1\bar{S}_0$. The terms of $S^+$ may be said to be produced by the coupling of an electron to $S^{++}$, and may be further subdivided into three groups —one proceeding from $^3P$, the second group proceeding from $^1\bar{D}_2$, the third from $^1\bar{S}_0$. Thus

$(S^{++}\ {}^3P)X_1$ gives us a Rydberg sequence of $^4P$ and $^2P$-terms, the values of which are

| | $N_1$ | $O_1$ | $P_1$ | $Q_1$ |
|---|---|---|---|---|
| $^4P_1$ .... | 75000 | 37000 | | |

$(S^{++}\ {}^1D_2)\,X_1$ gives us a Rydberg sequence of $^2D$-terms of which

| | $N_1$ | $O_1$ |
|---|---|---|
| $^2D_2$...... | 66000 | (22000) |

Sequences in $^2D$ have not been traced by Ingram. It is known from the work of Paschen on neon and of Russell and Saunders on the anomalous terms of Ca (*spectra of two valence elements*) that *terms arising from metastable states* form a Rydberg sequence of a displaced type, *i.e.*, when a certain number $x$ is added to them, $x$ representing the difference in value between the normal term and the metastable term of the higher ionised element. It is interesting to see if similar terms can be traced in the spectrum of $S^{+}$. Thus $^2D_2$ terms corresponding to the position of the valence electron in $X_1$ will form a Rydberg sequence of a displaced type. Hence $^2D_2$ of the $O_1$ state will have an approximate value of 22000 because the corresponding $^4P_1$ has a value of 37000 and we assume $^3P$ -- $^1D_2$ of $S^{++}$ to be about 15000. I tried to trace these terms and the following combinations were obtained :—

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* This line being 6 units off, measurements in this region are being repeated with a 10-foot grating mounted on the Paschen–Runge plan.

| | $^2F_3$ 89 | $^2F_4$ 431 | $^2D_2$ 41 | $^2D_3$ 2780 | $^2P_1$ 135 | $^2P_2$ |
|---|---|---|---|---|---|---|
| | (1) | | (3*ur*) | | | |
| $^2D_2$ | 25998·2 | | 25478·4 | ( ) | ( ) | ( ) |
| 38 | | | | | | |
| | (2) | (3*ur*) | (1*ur*) | (3*ur*) | | (4) |
| $^2D_3$ | 26038·6 | 25944·6 | 25514·0 | 25554·2 | | 22613·5 |

Further multiplets will be situated in the region λ 2500 Å. which has not yet been investigated.]

Thanks are due to Prof. Saha, of the Allahabad University, for guidance in this piece of work. The work was carried out at the Allahabad Physical Laboratory.

# *The Probability of Excitation by Electron-Impact in Neon.*

By R. d'E. Atkinson, M.A., D.Phil., Charlottenburg.

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The importance of "transition-probabilities" in modern physics is steadily increasing, and our knowledge of them has of late also made considerable progress; the values of several of them have now even been calculated directly by the wave-mechanics.* The probability of excitation of a quantum-jump by electron-impact is, however, a noticeably backward branch of the subject: not only is it as yet almost untouched by theory; the experimental determinations are also somewhat scanty, more especially in the case of the inert gases.

It is therefore of interest that some recent data of Townsend and McCallum† allow an estimate to be made in the case of neon. It is not indeed possible to obtain from them the probability of any definite excitation, but a sort of "average of the sum of all probabilities" can be evaluated with fair certainty. The problem has not been attempted by the authors, and appears in fact difficult to treat by methods hitherto published; the line here developed seems to be new.

The experimental method is identical in principle with that used in much previous work in the same laboratory, and the present discussion could be equally well applied to measurements on several other gases. The equations will therefore be put in a general form. There is, however, one distinction which prevents the analysis from being applicable in fact to any of the work which had previously appeared. The most prominent result of the latest paper is to justify a criticism levelled‡ against all the earlier work, namely, that the results were vitiated by the effects of impurities; the attainment of spectroscopic purity is now directly shown to be essential. Even in the latest work the precautions were not the usual ones, and the gas did not remain clean overnight; none the less it seems on the whole probable that they were just sufficient for the purpose, and this will be assumed here.

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* Schrödinger, 'Ann. Physik,' vol. 80, p. 489 (1926); Sugiura, 'J. Physique,' vol. 3, p. 113 (1927); Trumpy, 'Z. Physik,' vol. 50, p. 228 (1928).

† 'Phil. Mag.,' vol. 5, p. 695 (1928). (Quoted below as *loc. cit.*)

‡ *E.g.*, Atkinson, 'Roy. Soc. Proc.,' vol. 119, p. 335 (1928) (Quoted below as *loc. cit.*) *Cf.* also the statements of Townsend, *loc. cit.*, p. 699, and, apparently, 'Phil. Mag.,' vol. 45, p. 1071 (1923).

The essential details of the method may be briefly summarised as follows. A small initial current $i_0$ is set free photoelectrically from one of a pair of parallel plates. The electrons are accelerated towards the other one by a field (X) at such a pressure ($p$) that fresh electrons are produced in the gas, and the resulting total current $i$ depends on the distance between the plates, $x$. If X and $p$ are kept constant as $x$ varies, it is found that $i = i_0e^{\alpha x}$ in so far as the influence of positive-ion collisions can be neglected. It is also found that $\alpha/p = f(\mathrm{X}/p)$.

If we assume then that the increase of current is not due to impurities, but to genuine single-process ionisation of the neon atoms themselves, it follows that electrons, accelerated in neon at such pressures that they make a considerable number of collisions between 16·6 and 21·5 volts, nevertheless do sometimes reach velocities corresponding to the upper figure without suffering an inelastic collision. Thus the absolute probabilities of the inelastic collisions must be appreciably less than unity. This qualitative result is, of course, not new,* and there is no justification for assuming, as Prof Townsend and Dr. McCallum appear to do,† *that it is not in agreement with the quantum theory*.‡ The work which had established it, however, did not lend itself readily to quantitative treatment.

The above exponential equation does not hold at small values of $x$, and the explanation given is that the electron-stream must first become thoroughly complicated, so as to smoothe out all possible steps in the current-curve. As to the form of the velocity-distribution when the desired steady state is actually reached, the only definite suggestion by the authors of the experiments has been that it might approach a Maxwellian one. This has, however, not been insisted on; we shall find here that it is in general not very near the truth.

The question of the actual form of the distribution-function appears in fact to be much the most convenient point at which to attack the whole problem, for the following reason. If there were no losses of energy except at ionisation, and if ionisation always occurred as soon as the necessary energy was reached, the curve would take the form $i = i_0 2^{\mathrm{X}x/\mathrm{I}} = i_0e^{0\cdot693\mathrm{X}x/\mathrm{I}}$ (where I is the ionisation-potential); the experimental values of $\alpha$ are much smaller than 0·693X/I, and clearly the inelastic collisions are what act as a brake on the rise of current.* If, however, we attempt to assume a definite probability for these collisions, so as to reduce the exponent to the right amount, we still have to allow for the fact that an electron which actually suffers an inelastic collision has then, at subsequent planes, several volts more energy than one which succeeds in keeping its energy until it has enough to ionise; it will thus be in a position to ionise in its turn earlier than the other at the next attempt, and this will have a considerable secondary effect on the exponential constant. In this way the electron-groups continually break up, and it seems better to start by discussing *de novo* the whole question of the distribution of energies in the stream.

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* *Holst and Oosterhuis*, 'Physica,' vol. 1, p. 78 (1921).

† *Loc. cit.*, p. 699. *Cf.* also 'Phil. Mag.,' vol. 47, p. 738 (1924).

‡ The Quantum Theory position may be found, for example, in Franck and Jordan, "Anregung von Quantensprüngen durch Stösse," p. 180; "as is to be expected on theoretical grounds, . . . the efficiency [of excitation in the inert gases] is extremely small, expecially in Neon." Prof. Townsend and Dr. McCallum appear to have assumed that, *according to the Quantum Theory*, the efficiency is always nearly unity.

The argument will be founded on a principle already set forth,† that once the current-curve has become exponential, the entire distribution can be directly calculated if the electrical properties of the atoms are known, use being made merely of the theorem of the conservation of energy. For practical application of this principle it is necessary to postulate somewhat idealised atomic characteristics, but this is merely to reduce the purely algebraical difficulties. The problem will be treated first on very simple assumptions, and then on somewhat more complicated ones, and it will appear that further increase in complication along such lines can scarcely bring much further improvement in accuracy, owing to other difficulties.

As collisions at the various potentials are in no way distinguished from one another in the experiments, while theory is still hardly in a position to offer much help on the point, we leave on one side the question of the relative probabilities of different transitions and the changes of probability with potential. We assume arbitrarily that the total probability that an (unspecified) inelastic collision will occur is zero below the first critical potential F, and constant between this and the ionisation-potential I. For the sake of convenience we postulate that it is constant per centimetre of the field travelled, not per collision. The number of collisions per centimetre is somewhat uncertain, and is different at different energies, so that our assumption is probably preferable to, and certainly less complicated than, the assumption of a constant probability per collision. It may be noted that, since the number of possible transitions increases greatly with the voltage, while their individual probability presumably decreases, the hypothesis may actually be fairly close to the facts; but this is comparatively irrelevant. We have merely defined what we propose to understand by "average probability," and the results must be viewed in the light of the convention thus adopted.

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* That the photo-electric effects which they also call forth will be too small to be measured by this method is clear. (Atkinson, *loc. cit.*, p. 337.)

† Atkinson, *loc. cit.*, p. 344.

For a first calculation we will also assume that the probability of ionisation is large above the ionisation-potential. This simplification will be removed later.

It is convenient for the analysis to introduce also a slight change of notation. For the $\alpha$ of Townsend's formula we substitute $\omega = \alpha/X$; the equation thus becomes $i = i_0 e^{\omega V}$ if V is the potential between the plates, and the relation $\alpha/p = f(X/p)$ simplifies to $\omega = F(X/p)$. The pressure, which is entirely irrelevant except in so far as it affects $X/p$, thus no longer appears in any of the formulæ explicitly, and it is no longer necessary to "put $p = 1$ for simplicity." Further, for the case that inelastic collisions occur only at approximately one potential, and that some definite proportion of these result in "ionisation" (helium at high pressure with a trace of impurity, for example), the relation may be expected to reduce to $\omega = F = \text{const.}$, as in fact it approximately does in the range in which the "elastic" losses can be neglected. Since a departure from constancy is more striking than a departure from proportionality with the abscissa at small abscissæ, this form appears also better suited to make the effect of the elastic losses visible in the curves. However that may be, referring everything to a scale of volts instead of to one of centimetres is very much more convenient in the present treatment.

We consider now a plane, A, in the gas, perpendicular to the field-direction. Let $n \,.\, dV$ be the number of electrons with energies between I and $I + dV$ volts that cross this plane per second; this number divided by the number giving the total current across A must have the same value for all planes, since the distribution has reached a steady state. Thus at a point $I - V$ volts further down the field, where the total current is larger in the ratio $e^{(I-V)\omega}$, the number of electrons with energies in the same range must be $n \,.\, e^{(I-V)\omega} dV$. Consider now the electrons at A with energies between V and $V + dV$, where $F \gtreqless V \gtreqless I$; let their number be $n_V \,.\, dV$ per second. As these electrons travel down the field, their number will be diminished by occasional inelastic collisions that remove individual ones from the group; we have assumed that the probability of this is constant per centimetre, *i.e.*, per volt, and we accordingly have for the number of electrons still in the group when the group-energy has become V′, $n_V \,.\, e^{-(V'-V)\theta} dV$, where $\theta$ is the constant we wish to determine. Since there is no accumulation of electricity between any two planes, and since by the conservation of energy there is no other source of electrons of energy V′, this is the number of electrons of energy V′ crossing the plane A + V′ − V per second. In particular if we put V′ = I we have $n_V \, . \, e^{-(I-V)\theta} = n \, . \, e^{(I-V)\omega}$ or

$$n_V = n \, . \, e^{(I-V)(\theta+\omega)} \qquad (F \gtreqless V \gtreqless I).$$

The extension of the formula below the first critical potential obviously takes the form

$$n_V = n \, . \, e^{(I-F)\theta+(I-V)\omega} \qquad (0 \gtreqless V \gtreqless F).$$

Thus for the idealised conditions assumed here, the derivation of a complete expression for the distribution of velocities presents no great difficulty ; having obtained the formula, we have two distinct methods open to us of deducing an equation for the constant θ. The first is as follows.

The number of electrons with energies between 0 and $d$V volts is evidently $n \, . \, e^{(I-F)\theta+I\omega} \, dV$; this must be equal to the number that *will* be formed (each with energy 0), between the planes A and A + $d$V. This number is the sum of two ; on the one hand we have, as the result of ionising collisions, $2n$ (since the ionising electron is also reduced to rest), and on the other hand all those that will be produced by inelastic impacts at excitation potentials in this region. The number of these is

$$\int_F^I n_V \, . \, \theta \, dV = \frac{n\theta}{\theta+\omega}\left(e^{(I-F)(\theta+\omega)} - 1\right).$$

Thus we obtain as the equation for our unknown, θ,

$$\frac{\theta}{\theta+\omega}\left(e^{(I-F)(\theta+\omega)} - 1\right) + 2 = e^{(I-F)\theta+I\omega}.$$

For future reference this may be rewritten

$$e^{(I-F)\theta}\{\theta\,(e^{I\omega} - e^{(I-F)\omega}) + \omega e^{I\omega}\} = \theta + 2\omega,$$

which is also the most convenient form for evaluation.

It may be noted that, if we put θ = 0 in this equation, we obtain $I\omega = 0 \cdot 693$, as we evidently should.

The above derivation has been given first as being physically the more direct, since the part played by the probability-constant θ enters into it explicitly ; the following alternative derivation, in which that is not the case, is algebraically simpler. If we integrate $n_V$ from 0 to I, we obtain the total current, N, at the plane A.[*] The rate of increase of this, $d$N/$d$V, at A is clearly equal to $n$; it is also equal to $\omega N$, since the curve is exponential. If then in the expression for N we write $\omega N = n$, we obtain the above equation directly, though at first sight it is somewhat surprising that this should be so.

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[*] *I.e.*, the total electron-current. The total current of all sorts is, of course, the same at all planes, the balance being carried by positive ions. The total current when the movable electrode is in the plane A is the same as the electron-current at the plane A wherever the movable electrode is, unless the positive-ion space-charges distort the field.

In the case of the experiments under review, $\alpha$ was $4 \cdot 2$ when X was 483, and $4 \cdot 3$ when X was 487; we may thus put $\omega = 8 \cdot 76 \, . \, 10^{-3}$. Since the gas was neon we have also $F = 16 \cdot 6$ and $I = 21 \cdot 5$. The equation is then solved by $\theta = 0 \cdot 344$. Thus the inelastic collisions reduce the number of electrons in any group at the rate $1 : e^{-0 \cdot 344} = 1 : 0 \cdot 708$ per volt. If then there are $m$ collisions per volt, the efficiency is $1 - \sqrt[m]{0 \cdot 708}$ per collision.

The evaluation of the total number of collisions that occur, a necessary feature of any discussion of efficiencies, is quite extraordinarily difficult in the present case. The formula of Hertz,[*] $\nu dx = \frac{3x}{\lambda^2} \log \frac{a}{x} \, dx$, rests on two assumptions, neither of which is in any way fulfilled here. The first is that at the plane $x = a$ the density of the electrons under consideration is zero, as is the case when a collecting-plate is there. The condition is also satisfied when all the electrons suffer an inelastic collision as soon as they reach this plane for the first time, and we have assumed up to the present that this is the case as soon as they reach the energy I. The assumption is, however, certainly incorrect. Qualitatively it is clear that the real number of collisions will be larger than that given by the formula, since the electrons which have passed the plane where their energy was I can now return and suffer further collisions at lower potentials; it is however not very easy to estimate the effect of this possibility. The other unfulfilled assumption is that no serious number of inelastic collisions occurs within the range under consideration itself; since an electron which reaches, say, 20 volts has a larger chance of turning back and colliding at, say, 18 volts on Hertz' assumption than here, where it may lose its energy at 20 volts and be forced to travel forwards, this disturbance works in the opposite direction to the other. On the whole it appears probable that in this case the former effect predominated, and we shall allow for both together by putting the plane $x = a$ at $22 \cdot 5$ volts, and integrating Hertz' formula then from the plane $16 \cdot 6$ volts to the plane $21 \cdot 5$ volts. If we assume $\lambda = 1/11$ cm. at $p = 1$, this gives us 33 collisions in the range in question.[†]

The accuracy of our assumptions probably does not justify us in subdividing this number for the different voltages, and we may say we have nearly 7 collisions per volt. In this case the efficiency works out to 5 per cent. per collision. For convenience we append the values of the efficiency for some other values of $m$, the number of collisions per volt.

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[*] 'Z. Physik,' vol. 32, p. 305 (1925).

[†] $X/p$ was 13 in these experiments.

| $m$ = | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|
| E (per cent.) = | 10·9 | 8·3 | 6·7 | 5·6 | 4·8 | 4·2 | 3·8 | 3·4 |

We reserve discussion of these values, which at first sight may seem somewhat large, until the effect of assuming a smaller ionisation-probability than 1 in the evaluation of $\theta$ has been investigated.

The calculation is in this case considerably more complicated, but the simplifying assumptions necessary are very similar to the previous ones. We assume that the probability, $\phi d\mathrm{V}$, that an ionising-collision will occur between two planes distant $d\mathrm{V}$ apart is constant as soon as the electron's energy is greater than I, that the surplus energy is equally divided between the ionising electron and the new one produced, and that no inelastic collisions that do not lead to ionisation occur in this range. Since the probability per collision that ionisation will occur apparently rises with the energy, while the number of collisions per volt decreases, the assumption of a constant probability per volt may again be fairly near the truth.

The distribution of the electron-velocities at low values will now be modified by the fact that electrons join the stream with energies $> 0$. The value of $\phi$ is, however, certainly so large that the number joining with energies of, say, 12 volts or more is entirely negligible, and the distribution from this figure on will thus be as before. Accordingly we may proceed on the following lines.

Let P be some potential so large that no electrons with energy P join the stream. Then if the number of electrons at the plane A, with energy between I and I + $d\mathrm{V}$ is $n \,.\, d\mathrm{V}$ as before, the number which, on reaching the plane A + P − V will have the energy P is

$$e^{(\mathrm{P}-\mathrm{V})\omega}\, n \,.\, e^{(\mathrm{I}-\mathrm{F})\theta+(\mathrm{I}-\mathrm{P})\omega}\, d\mathrm{V} = n \,.\, e^{(\mathrm{I}-\mathrm{F})\theta+(\mathrm{I}-\mathrm{V})\omega}\, d\mathrm{V}.$$

This number is made up of two: on the one hand we have those which, at the plane A, already have the energy V; we call these $n_{\mathrm{V}}\, d\mathrm{V}$ as before: on the other hand we have all those which, at planes A + V′, come in with energies V + V′. The number of these is twice the number of ionising collisions with energies I + 2(V + V′) that occur in the planes A + V′. The number of electrons which at a plane A − (2V + V′) had the energy I was

$n \,.\, e^{-(2\mathrm{V}+\mathrm{V}')\omega}\; d\mathrm{V}$; since $\phi\, d\mathrm{V}' \,.\, e^{-2(\mathrm{V}+\mathrm{V}')\phi}$ of these come in question, we have

$$n_V\,dV = n \,.\, e^{(I-F)\theta + (I-V)\omega}\,dV - 2n\phi\,dV \int_0^P e^{-2(V+V')\phi - (2V+V')\omega}\,dV'$$

or

$$n_V = n \,.\, e^{(I-F)\theta + (I-V)\omega} - 2n \,.\, \phi e^{-2V(\phi+\omega)} \left[\frac{e^{-V'(2\phi+\omega)}}{2\phi+\omega}\right]_P^0 .$$

By hypothesis no electrons with energy P join the stream; thus it will make no difference if ∞ is substituted for P in the limits of this expression. A difficulty would arise if P were actually greater than F, and this might well occur with some gases at low pressures; with the lighter inert gases at fairly high pressures it can scarcely be the case. Thus we have

$$n_V = n \,.\, e^{(I-F)\theta + (I-V)\omega} - \frac{2n\phi \,.\, e^{-2V(\phi+\omega)}}{2\phi+\omega} \qquad (0 \gtreqqless V \gtreqqless F).$$

For the range of inelastic collisions we have as before

$$n_V = n \,.\, e^{(I-V)(\theta+\omega)} \qquad (F \gtreqqless V \gtreqqless I).$$

The new range $V \lesseqqgtr I$ can also be evaluated without difficulty. The number of electrons which, at a plane A — (V — I), had the energy I was $n \,.\, e^{-(V-I)\omega}\,dV$; of these, $e^{-(V-I)\phi}$ survive, and have the energy V. Thus

$$n_V = n \,.\, e^{(I-V)(\phi+\omega)} \qquad (I \gtreqqless V).$$

The total current at the plane A is thus

$$\int_0^C n_V\,dV = N$$

$$= \frac{n}{\omega} e^{(I-F)\theta}\left(e^{I\omega} - e^{(I-F)\omega}\right) - \frac{n\phi}{(2\phi+\omega)(\phi+\omega)}\left[e^{-2V(\phi+\omega)}\right]_F^C$$

$$+ \frac{n}{\theta+\omega}\left(e^{(I-F)(\theta+\omega)} - 1\right) + \frac{n}{\phi+\omega}.$$

The limit can again be raised to infinity, so that

$$N = \frac{ne^{(I-F)\theta}}{\omega}\left[e^{I\omega} - \frac{\theta}{\theta+\omega} \,.\, e^{(I-F)\omega}\right] - \frac{n}{\theta+\omega} + \frac{n}{2\phi+\omega}.$$

The number of new ionisations between A and A + $dV$ is

$$n\phi \int_I^\infty e^{(I-V)(\phi+\omega)} \,.\, dV = \frac{n\phi}{\phi+\omega},$$

and this must as before be ωN. Thus we obtain as our final equation

$$e^{(1-F)\theta}\{\theta(e^{1\omega}-e^{(1-F)\omega})+\omega e^{1\omega}\}=\omega+(\theta+\omega)\left[\frac{2\phi^2-\omega^2}{(2\phi+\omega)(\phi+\omega)}\right].$$

The earlier form is obtained, as it should be, by putting $\phi = \infty$, and we see that the present more complicated analysis gives a result differing from the previous one only by the factor in square brackets.

It will be found that $\phi$ can hardly be so small that this factor differs seriously from 1. For example, if we assume 4 *collisions* per volt, with an ionising efficiency of 22 per cent., or 3 collisions per volt with an ionising efficiency of 28·5 per cent. (figures which on the whole appear reasonably probable), we have $\phi = 1$; since $\omega = 8{\cdot}76 \,.\, 10^{-3}$, the correction is clearly negligible. Even if we put $\phi$ as low as 0·20 (which would mean only 6½ per cent. ionising efficiency with 3 collisions per volt, or 9½ per cent. with 2 collisions per volt), we still obtain $\theta = 0{\cdot}331$, giving an excitation-efficiency of 4·6 per cent. instead of the previous 4·8 per cent. for 7 collisions per volt. Clearly the uncertainties of the present analysis rest on the difficulty of applying the Hertz formula, and not in the particular assumptions on which we work. Thus there is no point in extending the discussion to take account of the facts that the surplus energy on ionisation is not in general equally divided between both electrons, or that there is also in general a small surplus energy with excitation-impacts.

A more precise application of the analysis would perhaps be possible if we definitely assumed a variation of $\theta$ with voltage, so as to take account roughly of the changing number of collisions per volt and the change (when known) of probability per collision; the necessary information is, however, hardly available as yet. It seems clear in any case that the result would not be much changed.

We are thus led definitely to the conclusion that the average value for the sum of all excitation-probabilities is about 5 per cent. in neon. In point of fact there will presumably be regions in the energy-range in question where the probability is appreciably less than the average; owing, however, to the high power to which the probability is raised (33 collisions in the entire range), such gaps can be compensated by a very slight increase in other regions. We have thus to consider the reasonableness of this figure.

On theoretical grounds, the high value of the excitation-potential and the high degree of symmetry of the unexcited atom lead us to expect a comparatively small excitation-probability. On experimental grounds the well-known ease with which a discharge can be passed through neon points to the same conclusion. As one of the best-known determinations of an excitation-probability is that for the 4·9-volt transition in mercury,[*] where the value is about 3½ per cent., it might be suggested that 5 per cent. is too high for neon. The following arguments may perhaps lend support to the figure.

In the first place we have to do here with the sum of all possible transition-probabilities; the number of possible transitions is large in neon, and any one individual probability will thus be decidedly less than 5 per cent., at least unless there is in fact a very marked variation of probability with voltage. In the second place, 2537 Å. is an intercombination line, with an optical intensity about 50 times less than that of the D-lines for example, and its electron-excitation ought therefore to be relatively improbable. The comparison should be *made with the most probable transitions* of other elements, and as far as measurements of these go, their probabilities seem to approach unity in many cases, if we exclude the inert gases.[†]

The readiness with which neon conducts may in part also be accounted for by two other factors. The first is that the mean free path in this gas is one of the longest among the simple gases[‡] (we are clearly not concerned here with very low velocities); the second is that $(I - F)/I$ has here a comparatively small value. Both these factors reduce the number of collisions that actually occur in the inelastic range; as this number is an exponent, the effect of altering it is considerable. (Differentiating the Hertz formula shows that the maximum number of collisions occurs at the plane $x = a/e$, *i.e.*, in our case at less than half the ionisation potential, and falls off steadily after that.)[§] Thus on the whole the figure here obtained may be nearly correct.

It may be noted that impurities must almost certainly raise the value of $\alpha$, *i.e.*, of $\omega$; a further decrease in the value of $\omega$ below that now found experimentally would involve an *increase* in the value of $\theta$, *i.e.*, of the excitation-probability.

The position thus reached throws some fresh light on the relations between the "Townsend Theory of Ionisation by Collision" and the general scheme provided by the Quantum Theory. The most recent unified presentation of the Townsend Theory appeared some time ago, and it seems certain that it has undergone alterations since then, though their extent is difficult to determine; central to it is, however, presumably still the derivation of the well-known and empirically verified "Townsend Collision Formula." This rests on the definition of the quantity $\alpha$ as "the average number of new ions produced per ion per centimetre in the direction of the field."* The present discussion has shown that the definition, and the derivation based on it, require some modification.

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[*] Sponer, 'Z. Physik,' vol. 7, p. 185 (1921); but see also Hertz, *loc. cit.*

[†] Franck and Jordan, p. 179.

[‡] See for example, Franck and Jordan, p. 20.

[§] In this respect the previous paper by Atkinson (*loc. cit.*, p. 342), contains an error; the number of collisions per volt does not rise steadily with the voltage, the average energy per collision is probably appreciably *less* than 19·77/2, and the agreement with experiment is thus greatly improved.

The measured $\alpha$ of the curves and the "average number of ions per ion per centimetre" would only be identical on the assumption, which was in fact originally made, that the probability of ionisation is independent of the distance travelled since the last ionisation, *i.e.*, as we now know, of the energy of the electron. In all other cases $\alpha$ must be multiplied by a factor depending on the integrals of the various probability functions concerned. For example, let the probability of ionisation be zero up to a certain potential, and then so large that ionisation occurs within a small energy-range; if the energy is not also dissipated in other ways, the average number of ions per ion per centimetre is then $\alpha/0{\cdot}693$. If nothing is known about the form of the probability-curves involved, the relation between the measured $\alpha$ and the "average number of ions per ion per centimetre" cannot be determined.

It is clear that an exponential current-curve will always be obtained as soon as the distribution of electronic velocities has reached its final chaotic form, and that in fact if inelastic collisions can occur at various energies this form will in general be fairly quickly reached. The curve does not, however, take the form $i = i_0 e^{\alpha x}$ because $\alpha$ has the meaning originally assigned to it, but for the fundamentally different reason that, in the notation of the present paper, $d\mathrm{N}/d\mathrm{V} = n$ (or nearly so), together with the fact that in the steady state $n/\mathrm{N}$ is constant. It is a question of principle whether we can in any degree name the electrons which are on the point of ionising, and the fact that we can appreciably increases the difficulty of the analysis.

It seems that previous treatments of this question may have led to somewhat unacceptable results partly because insufficient attention has been paid to this point. The most thorough attempt to infer ionisation-potentials from the values of $\alpha$ is by Townsend†; this treats the problem, however, in terms of the *average* energy possessed by *all* the electrons at any given plane, the *average* energy lost in a "cycle" by an electron, the *average* energy at which ionisations occur, and so on. It appears unlikely that a treatment as statistical as this can lead to correct results in a problem where various alternatives are often open to the electron, and in fact the results obtained are not confirmed by any other workers. Thus ionisation-potentials of 12* and 10† volts have been inferred for helium, 21 volts and 17 volts are given as "upper limits" for the ionisation-potentials of helium and neon respectively,‡ and the discovery that the losses at inelastic collisions have perfectly definite discrete values that can be predicted from optical data has no place in the statistical results at all. All that these measurements suggest is that, when the *average* energy of all the electrons is large, the average losses are also large enough to indicate a fair degree of average inelasticity.§

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* *E.g.*, Townsend, 'Phil. Mag.,' vol. 45, p. 446 (1923); Huxley, 'Phil. Mag.,' vol. 3, p. 1056 (1927), and vol. 5, p. 727 (1928), etc.

† 'Phil. Mag.,' vol. 45, p. 1071 (1923).

Notwithstanding these disagreements, however, the present analysis has shown that, if we trust to the very large and now almost completely unanimous mass of experiment that has established the supremacy of the quantum theory, so that we are clear as to the processes involved and the potentials at which they occur, the statistical experiments can give us, on the question of the probabilities of these processes, information which has not as yet been obtained by any other means.

One weakness of the present discussion should perhaps be specially mentioned. Not only is the energy gained on one mean free path in the field-direction somewhat more than 1 volt in neon when $X/p = 13$ as in the present case; it is possible that the phenomena are governed to an appreciable extent by the behaviour of the exceptional, rather than the average, electron. It will occasionally happen that electrons have a number of successive free paths longer than the mean, and a number of successive collisions which impose collectively very little motion against the field; it seems probable that the numbers of electrons that thus reach potentials very considerably above F may be much larger than they could be if each electron evinced only average behaviour. In an electron-stream increasing exponentially with the distance it is by no means clear that such effects will be counteracted at all accurately by other electrons differing from the average in the opposite sense. A calculation taking account of these considerations would probably be extremely complicated, but the possibility that they are important should not be forgotten.

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* 'Phil. Mag.,' vol. 45, p. 1078.

† Townsend and Ayres, 'Phil. Mag.,' vol. 47, p. 413 (1924).

‡ Townsend and Focken, 'Phil. Mag.,' vol. 2, p. 495 (1926).

§ Townsend and Bailey, 'Phil. Mag.,' vol. 44, p. 1045 (1922), and vol. 46, p. 661 (1923).

### *Summary.*

Starting from the Quantum Theory standpoint, a method is developed of analysing the results obtained by the Townsend type of experiment, in which currents of the form $i = i_0 e^{ax}$ are found on varying the distance $x$ between two parallel plates in a gas at comparatively high pressures. The first critical potential and the ionisation potential are assumed to be already known, and the mean probability that at potentials in the range between them a collision, if it occurs, will be inelastic can then be approximately evaluated. The chief uncertainty is due to the fact that the Hertz formula cannot strictly be employed here to calculate the total number of collisions that occur.

The result is applied to new measurements on neon by Townsend and McCallum, and the mean probability that collisions will be inelastic is found to be about 5 per cent. This represents the sum of the probabilities of *all* the transitions that can occur at any one given energy. Reasons are adduced for considering this figure a plausible one.

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# *The Ultra-Violet Spectrum of Magnesium Hydride.*

## 1.—*The Band at* λ 2430.

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(Communicated by A. Fowler, F.R.S.—Received October 26, 1928.)

[Plate 9.]

### *Introductory.*

The system of bands in the visible region of the emission spectrum of magnesium hydride is now well known. The bands with heads at λλ 5622, 5211, 4845 were first measured by Prof. A. Fowler,* who arranged many of the strongest lines in empirical series for identification with absorption lines in the spectra of sun-spots. Later, Heurlinger† rearranged these series in the now familiar form of P, Q and R branches, and considered them, with the OH group, as typical of doublet systems in his classification of the fine structure of bands. More recently, W. W. Watson and P. Rudnick* have remeasured these bands, using the second order of a 21-foot concave grating, and have carried out a further investigation of the fine structure in the light of the present theory of band spectra. Their detection of an isotope effect of the right order of magnitude,† considered with the general structure of the system, and the experimental work on the production of the spectrum‡, seems conclusive in assigning these bands to the diatomic molecule MgH. The ultra-violet spectrum of magnesium hydride is not so well known. The band at λ 2430 and the series of double lines in the region λ 2940 to λ 3100, which were recorded by Prof. Fowler in 1909 as accompanying the group of bands in the visible region, appear to have undergone no further investigation. In view of the important part played by hydride band spectra in the correlation of molecular and atomic electronic energy levels, it was thought that a study of these features might prove of interest in yielding further information on the energy states of the MgH molecule. The present paper deals with observations on the band at λ 2430; details of an investigation of the other features of the ultra-violet spectrum will be given in a later communication.

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* 'Phil. Trans.,' A, vol. 209, p. 447 (1909).

† 'Dissertation,' Lund (1918).

## *Experimental.*

The source used for production of the spectrum was a magnesium arc in hydrogen at low pressure. The apparatus employed was very similar to that described by Prof. Fowler except that the pole-pieces were water-cooled to allow continuous running for long exposures. Hydrogen from a commercial cylinder was dried by passage over $P_2O_5$ and allowed to pass in a slow stream through the arc chamber, in which the pressure was usually kept between 1 to 5 cm. of mercury.

For a general survey of the spectrum thus produced photographs were taken on a quartz spectrograph (Hilger's E.2) giving a dispersion varying from 65 A./mm. at λ 5500 to 7·5 A./mm. at λ 2300. The most conspicuous features shown on these plates, apart from the series spectra of Mg and $Mg^+$ which are always present with varying relative intensity, are (1) the clearly defined set of heads of the visible band system; (2) the band structure at λ 2430, which in the general arrangement of its heads and in their intensity distribution closely resembles the 0, 0 sequence (at λ 5211) of the first system ; and (3) the almost continuous background of very close lines stretching throughout the whole of the intervening region. This background, without showing any conspicuous heads, appears to reach a maximum intensity in the region λ 3100 to λ 3500. The structure also becomes more open near this region, and between λ 2940 to λ 3100 has the appearance of series of double lines as described by Prof. A. Fowler. Heads, composed of relatively weak lines, may also be detected approximately at λλ 2640, 2720, 2940 and 3100. These evidently belong to a very extensive system of bands quite different in character from the other two systems, for in this case each band shows a single R-head and is degraded to the red end of the spectrum, whereas the other bands show strong P and Q-heads and are degraded to the further ultra-violet. It will be convenient in what follows to refer to these three systems as the α, β and γ-systems respectively. For the present, attention will be confined to the structure of the band at λ 2430, which is the only strong member of the β-system.

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* 'Astrophys. J.,' vol. 63, p. 20 (1926); 'Phys. Rev.,' vol. 29, p. 413 (1927).

† For further details of the isotope effect see Section 8 of the article by Loomis, chap. V, of the U.S. National Research Council Report on Molecular Spectra in Gases.

‡ A summary of the experimental work previous to 1909 is given in Prof. Fowler's paper, *loc. cit.*

### *Measurements.*

For the purpose of measurement, photographs of the β-system were taken on a quartz spectrograph of the Littrow type (Hilger's E.1) having a dispersion of 2·3 A./mm. in the region of λ 2400. The wave-lengths of certain strong lines were determined by interpolation using an iron arc comparison spectrum, taking Burns' measures as standard. The other lines were then measured relative to these on the strongest part of another plate which showed exceptionally good definition, and on which the overlapping γ-system was very weak. It was thought that in this way better relative values of the wave-lengths—so important in forming the combination differences, would be obtained, although possibly the absolute values might suffer slightly. Reductions to wave-numbers in vacuo were made with the aid of Kayser's 'Tabelle der Schwingungzahlen.' The wave-numbers of the P, Q, and R branches of the λ 2430 band are shown in Table I. A further Q-branch belonging to the next band of the sequence was sufficiently strong for measurement, and is shown in Table II, but no corresponding R or P branch could be detected. These appear to be abnormally weak if not altogether absent. Eye-estimates of the intensities of the lines are given in brackets after the wave-numbers. These were made in the first place from the plate using a microscope and then their order was checked by sliding one-half of an enlarged print of the band over the other half, and comparing line with line. The second method was especially useful for comparing lines of similar intensity which could not be brought into the field of view of the microscope at the same time. A complete list of the wave-lengths measured is given in Table VI.

Table I.—Wave-numbers and Intensities of the Lines of the Band near λ 2430.

| *m*. | P branch. | | Q branch. | | R branch. | |
|---|---|---|---|---|---|---|
| | $\nu$ (vac.). | (*i*). | $\nu$ (vac.). | (*i*). | $\nu$ (vac.). | (*i*). |
| 1 | | | | | 41248·62 | (2) |
| 2 | | | 41230·98 | (6) | (60·0<br>61·8) | |
| 3 | 41214·16 | (0) | 36·98<br>38·65 | (6)<br>(6) | (74·7) | |
| 4 | 04·39<br>02·55 | (1)<br>(1) | 40·18 | (6D) | 89·20 | (4) |
| 5 | 41194·55 | (2D) | 42·69 | (8) | 41304·10 | (4) |
| 6 | 86·18 | (2) | 46·36 | (9) | 20·15 | (5) |
| 7 | 78·64 | (3) | 50·64 | (9) | 36·57 | (5) |
| 8 | 71·89 | (4) | 55·67 | (10) | 53·91 | (5) |
| 9 | 65·95 | (5) | 61·44 | (10) | 71·92 | (4) |
| 10 | 60·82 | (5) | 67·98 | (9) | 90·35 | (1) |
| 11 | 56·54 | (4) | 75·07 | (10) | | |
| 12 | 52·52 | (D) | 83·30 | (8) | | |
| 13 | | (2D) | 91·81 | (7) | | |
| 14 | | | 41301·26 | (7) | | |
| 15 | | | 11·49 | (6) | | |
| 16 | | | 22·39 | (6) | | |
| 17 | | | 34·30 | (5) | | |
| 18 | | | 46·69 | (4) | | |
| 19 | | | 60·02 | (3) | | |
| 20 | | | 74·09 | (3) | | |
| 21 | | | 88·85 | (3) | | |
| 22 | | | 41404·69 | (2) | | |
| 23 | | | 21·15 | (2) | | |
| 24 | | | 38·66 | (6) | | |

The wave-numbers, given in brackets, for R (2) and R (3) were obtained by combining the values of $\Delta_2F''(3)$ and $\Delta_2F''(4)$ for the λ 5211 band with P (4) and P (5). D indicates that the line appears rather wide, possible double.

Table II.—Q-branch of (1, 1) Band.

| $\nu$ vac. | $\Delta\nu$. | $\Delta^2\nu$. |
|---|---|---|
| 41428·20 (1) | | |
| | 1·66 | |
| 29·86 (1) | | 0·15 |
| | 1·81 | |
| 31·67 (1) | | 1·39 |
| | 3·20 | |
| 34·87 (2) | | 0·59 |
| | 3·79 | |
| 38·66 (6) | | 1·01 |
| | 4·80 | |
| 43·46 (2) | | 0·97 |
| | 5·77 | |
| 49·23 (3D) | | 0·97 |
| | 6·74 | |
| 55·97 (3D) | | 0·18 |
| | 6·92 | |
| 62·89 (3) | | 1·33 |
| | 8·25 | |
| 71·14 (2) | | 0·73 |
| | 8·98 | |
| 80·12 (2) | | 0·99 |
| | 9·97 | |
| 41490·09 (3) | | 0·81 |
| | 10·78 | |
| 41500·87 (2) | | 1·02 |
| | 11·80 | |
| 12·67 (4) | | 0·77 |
| | 12·57 | |
| 25·24 (1) | | 1·08 |
| | 13·65 | |
| 38·89 (4) | | 1·17 |
| | 14·82 | |
| 53·71 (1) | | 0·34 |
| | 15·16 | |
| 68·87 (1) | | 1·80 |
| | 16·96 | |
| 85·83 (1) | | 0·19 |
| | 17·15 | |
| 41602·98 (1) | | |

### *The Structure of the Band.*

The band at λ 2430, shown in Plate 9, resembles the one at λ 5211 in possessing P, Q and R-branches, of which the Q are much the strongest. The branches are probably also double. The evidence for this rests chiefly with the first members of the P-branch; P (4) is clearly double, while P (5) is rather wider than the lines following it. Q (3) should show a doubling similar to P (4), but accurate verification of this is difficult owing to the superposition of Q (2) on one of the components. Q (4) like P (5) appears rather wide. The corresponding R lines cannot be well observed as they fall into positions occupied by strong Q lines. Thus, the very strong line Q (9) appears where the doublet

R (2) would be expected, and similarly Q (11) obscures R (3). The doubling appears to be similar to that of the λ 5211 band in decreasing rapidly in separation with increasing *m*, but to be on a smaller scale. From the width of the lines the doublet separation of higher members may be estimated to be $<0\cdot8$ cm.$^{-1}$. In the case of the λ 5211 band the normal separation lies between 1·5 and 2·0 cm.$^{-1}$ but increases for the lowest values of *m* to 4·5 cm.$^{-1}$ at P (5), which is the first member showing both components.

A curious feature of the band is the rapid decline of intensity in the P and R branches after passing the maximum value. In the P branch P (10) is very strong, P (11) is slightly weaker and then P (12) much weaker and rather diffuse. It was first thought possible that the diffuseness might be caused by near proximity of P (13) and an attempt was made to measure the line as two close lines. It was found, however, that the mean value formed a more natural continuation of the series and also gave a value of $\Delta_2F''$ (11)

Table III.—Comparison of the Combination Differences relating to the Final States of the λ 2430 and λ 5211 Bands.

| *m.* | λ 2430. | | | λ 5211. | | |
|---|---|---|---|---|---|---|
| | $\Delta_1F''$ (*m*). | | $\Delta_2F''$ (*m*). | $\Delta_1F''$ (*m*). | | $\Delta_2F''$ (*m*). |
| | (Q − P). | (R − Q). | (R − P). | (Q − P). | (R − Q). | (R − P). |
| 1 | | 11·64 | | 11·65 | 11·97 | |
| 2 | 22·82 | ... | 34·46 | 23·03 | 22·98 | 35·02 |
| 3 | 34·43<br>34·17 | — | — | 34·45 | 34·12 | 57·43 |
| 4 | 45·63 | 46·51 | ... | 46·04 | 45·88<br>45·50 | 80·16 |
| 5 | 56·51 | 57·74 | 103·02 | 57·02<br>57·14 | 57·13<br>57·45 | 102·90<br>102·64 |
| 6 | 67·72 | 69·51 | 125·46 | 68·54<br>68·28 | 68·43<br>68·74 | 125·67<br>125·73 |
| 7 | 78·75 | 80·90 | 148·26 | 79·49<br>79·53 | 79·78<br>80·01 | 147·92<br>148·27 |
| 8 | 89·72 | 92·47 | 170·62 | 91·06<br>91·82 | 90·90<br>91·26 | 170·84<br>170·83 |
| 9 | 100·62 | 103·94 | 193·09 | 102·27<br>101·96 | 102·10<br>102·50 | 193·17<br>193·22 |
| 10 | 111·44 | | 215·38 | 113·36<br>112·99 | 113·46<br>113·56 | 215·46<br>215·49 |
| 11 | 122·55 | | 237·83 | 124·22<br>124·00 | 124·50<br>124·53 | 237·68<br>237·56 |
| 12 | | | | 135·20<br>135·12 | 135·35<br>135·66 | 259·70<br>259·65 |

Table IV.—Comparison of the Combination Differences relating to the Initial States of the λ 2430 and λ 5211 Bands.

| $m$. | λ 2430. | | | λ 5211. | | |
|---|---|---|---|---|---|---|
| | $\Delta_1F'(m)$. | | $\Delta_2F'(m)$. | $\Delta_1F'(m)$. | | $\Delta_2F'(m)$. |
| | (Q − P). | (R − Q). | (R − P). | (Q − P). | (R − Q). | (R − P). |
| 1 | | | | 14·22 | 14·54 | |
| 2 | 24·49 | | | 25·37 | 25·30 | 39·52 |
| 3 | 36·71 | | | 37·24 | 36·91 | 62·28 |
| 4 | 48·14 | 49·02 | | 48·97<br>48·12 | 48·81 | 86·05 |
| 5 | 60·18 | 61·41 | 109·55 | 60·95<br>60·18 | 61·06<br>61·49 | 110·03<br>108·61 |
| 6 | 72·00 | 73·79 | 133·97 | 73·08<br>72·39 | 72·97<br>72·85 | 133·92<br>133·03 |
| 7 | 83·78 | 85·93 | 157·93 | 84·47<br>84·42 | 84·76<br>84·80 | 157·84<br>157·29 |
| 8 | 95·49 | 98·24 | 182·02 | 96·92<br>96·38 | 96·76<br>96·82 | 181·23<br>181·24 |
| 9 | 107·16 | 110·48 | 205·97 | 108·71<br>108·25 | 108·54<br>108·79 | 205·46<br>205·17 |
| 10 | 118·53 | | 229·53 | 120·35<br>120·16 | 120·45<br>120·73 | 229·16<br>228·98 |
| 11 | 130·78 | | | 132·04<br>(131·80) | 132·32<br>132·33 | 252·67<br>252·49 |
| 12 | | | | 143·84<br>143·46 | 143·99<br>(144·00) | 276·03<br>275·80 |

Where the components of the lines concerned are resolved there are two values of $\Delta F(m)$ for each value of $m$. In the above table such values are bracketed together, the ones arising from the low frequency components being placed first. In the case of the λ 5211 band the early single values arise from low frequency components as these are the stronger near the origin.

in close agreement with that given by the λ 5211 band.* The existence of a P (13) line is also rendered unlikely by examination of the R-branch. Here R (10), which has the same initial level as P (12), although rather close to Q (21) is clearly present, and like P (12) shows a drop in intensity. R (11), which corresponds to P (13), would be expected to appear in a space clear of other lines but cannot be observed. The Q-branch, however, does not show a similar break but continues with gradually diminishing intensity to Q (24), after which the lines become difficult to trace owing to the superposition of lines of the next Q-branch. A similar abrupt cessation of the P and R-branches has been noted by Mulliken† in the λ 3534 band of CaH. This band, however, has no Q-branch.

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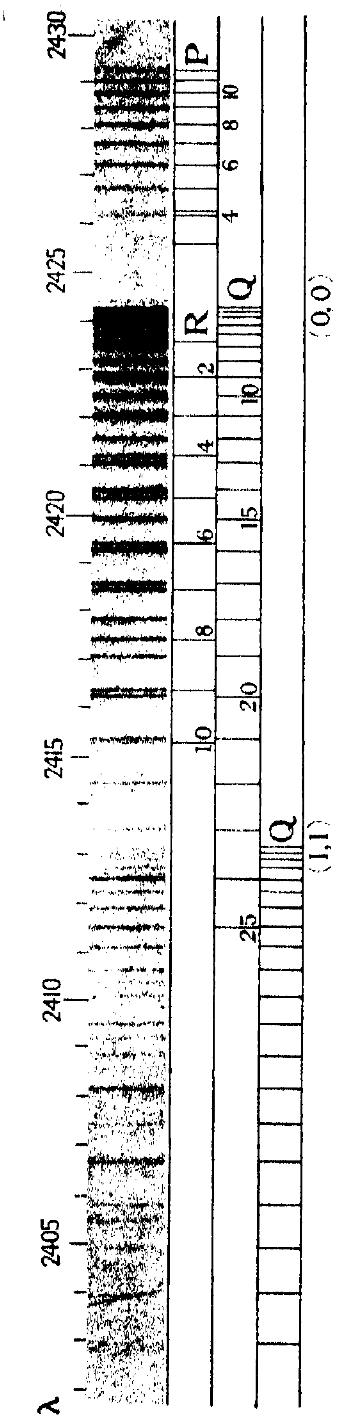
* For definition of $\Delta_2F''(m)$ see next section (equation (9)).

† 'Phys. Rev.,' vol. 25, p. 509, and vol. 25, p. 509 (1925).


2430
2425
2420
2415
2410
2405
λ
P
10
8
6
4
R
2
4
6
8
10
Q
10
15
20
25
(0,0)
Q
(1,1)

(*Facing p.* 448.)

### *Analysis of Band Structure.*

In Tables III and IV are shown the combination differences relating to the final and initial states of the λ 2430 band, together with the corresponding values obtained by W. W. Watson and P. Rudnick for the λ 5211 band. In order to facilitate comparison, the $m$-numbering used by those writers has been adopted here. The integral $m$ is not to be considered as a quantum number but as a counting number arising in the empirical ordering of the band lines. The $m$ values in the three branches are related according to the following equations :—

$$\mathrm{P}(m) = \mathrm{F}'(m-1) - \mathrm{F}''(m), \tag{1}$$

$$\mathrm{Q}(m) = \mathrm{F}'(m) - \mathrm{F}''(m), \tag{2}$$

$$\mathrm{R}(m) = \mathrm{F}'(m+1) - \mathrm{F}''(m). \tag{3}$$

The rotational term differences are defined in the usual way, thus :—

$$\Delta_1\mathrm{F}(m) = \mathrm{F}(m+1) - \mathrm{F}(m), \tag{4}$$

$$\Delta_2\mathrm{F}(m) = \mathrm{F}(m+1) - \mathrm{F}(m-1). \tag{5}$$

Two values of $\Delta_1\mathrm{F}(m)$ may be obtained from combinations of equations (1), (2) and (3) for each of the electronic states ; for the initial state

$$\Delta_1\mathrm{F}'(m) = \mathrm{R}(m) - \mathrm{Q}(m) = \mathrm{Q}(m+1) - \mathrm{P}(m+1). \tag{6}$$

and for the final state

$$\Delta_1\mathrm{F}''(m) = \mathrm{R}(m) - \mathrm{Q}(m+1) = \mathrm{Q}(m) - \mathrm{P}(m+1). \tag{7}$$

The value of $\Delta_2\mathrm{F}(m)$ for each state is obtained from the following combinations of the P and R branches

$$\Delta_2\mathrm{F}'(m) = \mathrm{R}(m) - \mathrm{P}(m) \tag{8}$$

$$\Delta_2\mathrm{F}''(m) = \mathrm{R}(m-1) - \mathrm{P}(m+1). \tag{9}$$

With this scheme of numbering the components of the doublets each receive the same $m$-number, and therefore the combination differences arising from the separate components also receive the same $m$-number and are bracketed together in the tables.

A study of these rotational term differences shows the following results. For the final level the values of $\Delta_2\mathrm{F}''(m)$ for the two bands are in close agreement over the range observed, while for the initial level the values of $\Delta_2\mathrm{F}'(m)$ are consistently larger in the case of the λ 2430 band. The $\Delta_1\mathrm{F}(m)$ values for the λ 2430 band show a marked combination defect ; the R − Q values being considerably larger than the corresponding Q — P values,—the difference increasing regularly with increasing values of *m*. Watson and Rudnick report a similar combination defect in the branches of the λ 5211 band for high values of *m*, but the differences in that case are much smaller. Similar combination defects appear in Kratzer's analysis of some of the CH bands* and in Watson's interpretation of the OH bands.† Where such combination defects occur, the R — P differences only can be used in comparing the terms of different bands, since the Q branches do not arise from the same initial levels as the corresponding P and R branches and, therefore, equation (2) cannot be combined with equations (1) and (3).

### *Interpretation of Band.*

The rotational term differences indicate that the final level of the band is the same as that of the λ 5211 band of the visible system. The latter band has been shown by Watson and Rudnick to be the 0, 0 vibrational band of its system, which Mulliken attributes to a $^2P \rightarrow {}^2S$ transition in the MgH molecule. Therefore, the λ 2430 band is due to a transition to the vibrationless state of the same $^2S$ level. Further, since the band is the first member of its sequence and no related bands of comparable intensity appear in the neighbouring regions of the spectrum, its initial vibrational quantum number is also very probably zero. The initial electronic state is probably to be classed as $^2P$, since the existence of a strong Q-branch excludes the possibility of the transition being of the type $^2S \rightarrow {}^2S$. This interpretation is supported by the great similarity of the structure and the intensity distribution of the λ 5211 and λ 2430 bands. Further, since no other bands of similar structure appear in the intervening region of the spectrum, the $^2P$ level here involved is presumably the next above that giving rise to the visible (α) system. If this interpretation is the correct one it is interesting to note that the doublet separation in the higher level is less than that for the lower level, as in the case of the corresponding atomic levels.

Many writers‡ have shown that the electron levels in a molecule show a marked similarity to the electron levels in the atom containing two electrons less than the total number in the molecule. The atom thus corresponding to the molecule MgH is Na. In the figure the electron levels of MgH and Na are drawn to scale for comparison.

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* 'Z. Physik,' vol. 23, p. 298 (1924).

† 'Astrophys. J.,' vol. 60, p. 145 (1924).

‡ R. S. Mulliken, 'Proc. Nat. Acad. Sci.,' vol. 12, p. 144 (1926), 'Phys. Rev.,' vol. 28, p. 481 (1926), and vol. 29, p. 391 (1927); R. Mecke, 'Z. Physik,' vol. 28, p. 261 (1924); R. T. Birge, 'Nature,' vol. 117, p. 300 (1926), 'Phys. Rev.,' vol. 28, p. 1157 (1926).

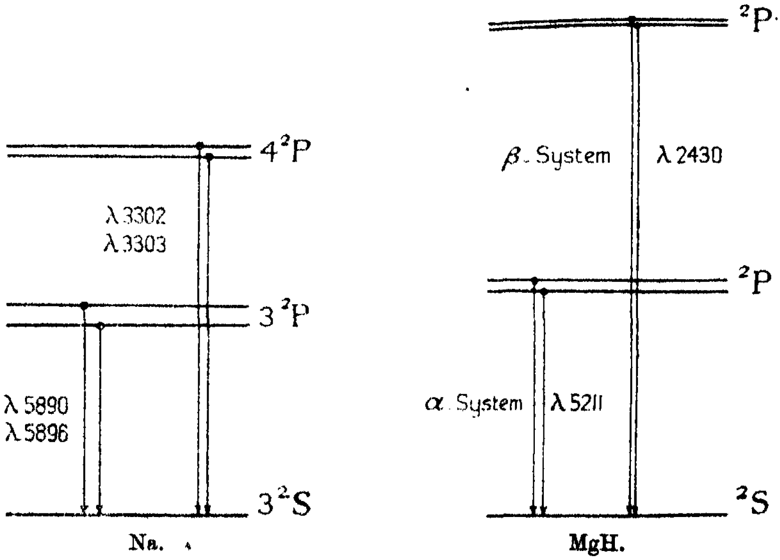

Fig.—Comparison of the electronic levels in the Na atom and the MgH molecule. The diagrams are to scale except for the doublet separations which have been increased about 100 times.

In this connection it was thought of interest to see whether the analogy between the molecular and atomic electronic energy levels could be carried a step further. Thus if the two $^2P$ levels associated with the α- and β-systems resemble consecutive members of a Rydberg sequence then a third system would be expected to appear in the region of λ 2000.

In order to test this point photographs were taken on a small quartz spectrograph (Hilger's E.31), using plates coated with paraffin. In this way the spectrum was obtained as far into the ultra-violet as λ 1850, using exposures up to 1 hour. In no case, however, was this further system detected although the pressure of hydrogen and the current through the arc were varied considerably. Thus, if a third $^2P \rightarrow {}^2S$ system occurs in this region at all, it is only with such feeble intensity that it is not perceptible against the faint background of the γ-system.

### *The Combination Defect.*

The combination defect is best considered in the light of Mulliken's application of Hund's theory of electron spin to the interpretation of the fine structure of band spectra.* According to this theory the multiplicity of an electronic level is determined by the resultant angular momentum of spin $s$ of the electrons; the multiplicity $r$ being equal to $2s + 1$. In the case of a doublet system, as here considered, $s = \frac{1}{2}$. For every value of $j_k$ the resultant of the orbital and nuclear angular momenta, there are then two rotational states, $F_1$ and $F_2$, arising from parallel and anti-parallel orientation of $s$ with respect to $j_k$. If the component of the orbital angular momentum parallel to the nuclear axis ($\sigma_k$) is zero (S states), each of these rotational states is single; if $\sigma_k$ is $> 0$ ($\sigma_k = 1, 2, 3, \ldots$, for P, D, F, . . . states) each is divided into two sub-states. If in two electron levels corresponding sub-states are called A and B sub-states, then the R and P branches result from A → A or B → B transitions, and the Q branches from A → B or B → A transitions (so called Q "crossing over"). In a transition to the $^2S$ state, since only one set of these levels is present in the final state, it follows that the P and R lines originate in one set of levels while the Q lines originate in the other. The combination defect is thus a measure of the difference between the A and B sub-states of the initial level. That the combination defect arises in the initial state is clearly shown in the present instance, since the defect is small in the $\alpha$-system, and large in the $\beta$-system, and therefore cannot be associated with the common $^2S$ level. It appears that in the case of these levels of MgH the difference between the A and B sub-states increases from one $^2P$ state to the next higher $^2P$ state. It also increases with increasing value of $j_k$. The fact that the Q-branch continues to much higher values of $m$ than the P and R branches suggests that in some way the sub-states from which it arises are more stable than those associated with the P and R branches. The apparent absence of P and R branches in the 1, 1 band also seems to support this.

### *Vibrational States.*

The search for further bands of the system of low intensity was rendered difficult by the overlapping of the very extensive $\alpha$-system. On the Hilger E.1 plates this was usually strong. But, with the instrument of lower dispersion greater variation in the relative intensities of the two systems was obtained, as the averaging effect of a long exposure was avoided, and on one plate measurements of the Q-heads of three neighbouring bands were possible. The results are shown in Table V, together with the wave-numbers of the Q-heads of the

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* For a brief account of Hund's theory see section 5 of Kemble's article, chap. VII, of the U.S. National Research Council Report on 'Molecular Spectra in Gases'; see also R. S. Mulliken, 'Phys. Rev.,' vol. 29, p. 637 (1927). For a general notation and examples of its application see R. S. Mulliken, 'Phys. Rev.,' vol. 30, p. 785 (1927).

## Table V.

Wave-numbers of Q-heads of the β-system.

| $n'$ \ $n''$ | 0 | | 1 | | 2 |
|---|---|---|---|---|---|
| 0 | 41237<br>(2424·3) | *1429* | 39808<br>(2511·3) | | |
| | *1624* | | *1620* | | |
| 1 | 42861<br>(2332·4) | *1433* | 41428<br>(2413·1) | *1367* | 40061<br>(2495·4) |

[The wave-lengths of the Q-heads observed are placed in brackets under the corresponding wave-numbers.]

Wave-numbers of Q-heads of the α-system.

| $n'$ \ $n''$ | 0 | | 1 | | 2 |
|---|---|---|---|---|---|
| 0 | 19271 | *1431* | 17840 | *1368* | 16472 |
| | *1534* | | *1534* | | *1534* |
| 1 | 20805 | *1431* | 19374 | *1368* | 18006 |

corresponding bands of the α-system, calculated from the formula given by Watson* :—

$$\nu_0 = 19217 + 1603\cdot5\,(n'+\tfrac{1}{2}) - 34\cdot75\,(n'+\tfrac{1}{2})^2 - 1493\cdot5\,(n''+\tfrac{1}{2}) + 31\cdot25\,(n''+\tfrac{1}{2})^2,$$

where $n'$ and $n''$ are given integral values.

It will be seen that the wave-number intervals corresponding to the final states of the two systems show good agreement. In the initial state the intervals are considerably larger for the β-system. This agrees with the result obtained from examination of the rotational data. Also, as pointed out by Birge and Mecke in the case of many other bands, the rotational constant B, of which the $\Delta_2F(m)$ values are a measure, increases with increase of the vibrational constant $\omega_0$.

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* 'Phys. Rev.,' vol. 27, p. 801 (1926).

Table VI.—List of Wave-lengths Measured.

| λ (I.A.). | $\nu_{\text{vac.}}$ | Classification and remarks. |
|---|---|---|
| 2429·247 (2D) | 41152·52 | (0, 0) P (12). |
| 29·010 (4) | 56·54 | (0, 0) P (11). |
| 28·757 (5) | 60·82 | (0, 0) P (10). |
| 28·455 (5) | 65·95 | (0, 0) P (9). |
| 28·104 (4) | 71·89 | (0, 0) P (8). |
| 27·706 (3) | 78·64 | (0, 0) P (7). |
| 27·262 (2) | 86·18 | (0, 0) P (6). |
| 26·768 (2D) | 94·55 | (0, 0) P (5). |
| 26·297 (1) | 41202·55 | (0, 0) P (4). |
| 26·189 (1) | 04·39 | |
| 25·730 (00) | 12·18 | |
| 25·596 (0) | 14·46 | (0, 0) P (3). |
| 24·400 (1) | 34·79 | (0, 0) Q (1) ? |
| 24·271 (6) | 36·98 | (0, 0) Q (2), (0, 0) Q (3) long wave compt. |
| 24·178 (6) | 38·56 | (0, 0) Q (3) short wave compt. |
| 24·083 (6D) | 40·18 | (0, 0) Q (4). |
| 23·936 (8) | 42·69 | (0, 0) Q (5). |
| 23·720 (9) | 46·36 | (0, 0) Q (6). |
| 23·588 (2) | 48·62 | (0, 0) R (1). |
| 23·468 (9) | 50·64 | (0, 0) Q (7). |
| 23·173 (10) | 55·67 | (0, 0) Q (8). |
| 22·834 (10) | 61·44 | (0, 0) Q (9). Masks compts. of (0, 0) R (2). |
| 22·450 (9) | 67·98 | (0, 0) Q (10). |
| 22·034 (10) | 75·07 | (0, 0) Q (11), (0, 0) R (3) superposed. |
| 21·551 (8) | 83·30 | (0, 0) Q (12). |
| 21·205 (4) | 89·20 | (0, 0) R (4). |
| 21·052 (7) | 91·81 | (0, 0) Q (13). |
| 20·498 (7) | 41301·26 | (0, 0) Q (14). |
| 20·332 (4) | 04·10 | (0, 0) R (5). |
| 19·899 (6) | 11·49 | (0, 0) Q (15). |
| 19·392 (5) | 20·15 | (0, 0) R (6). |
| 19·260 (6) | 22·39 | (0, 0) Q (16). |
| 18·563 (5) | 34·30 | (0, 0) Q (17). |
| 18·430 (5) | 36·57 | (0, 0) R (7). |
| 17·838 (4) | 46·69 | (0, 0) Q (18). |
| 17·416 (5) | 53·91 | (0, 0) R (8). |
| 17·060 (3) | 60·02 | (0, 0) Q (19). |
| 16·364 (4) | 71·92 | (0, 0) R (9). |
| 16·237 (3) | 74·09 | (0, 0) Q (20). |
| 15·375 (3) | 88·85 | (0, 0) Q (21). |
| 15·288 (1) | 90·35 | (1, 0) R (10). |
| 14·451 (2) | 41404·69 | (0, 0) Q (22). |
| 13·493 (2) | 21·15 | (0, 0) Q (23). |
| 13·080 (1) | 28·20 | (1, 1) Q. |
| 12·984 (1) | 29·86 | (1, 1) Q. |
| 12·879 (1) | 31·67 | (1, 1) Q. |
| 12·692 (2) | 34·87 | (1, 1) Q. |
| 12·471 (6) | 38·66 | (0, 0) Q (24), (1, 1) Q. |
| 12·192 (2) | 43·46 | (1, 1) Q, |
| 11·856 (3D) | 49·23 | (1, 1) Q. |
| 11·464 (3D) | 55·97 | (1, 1) Q. |
| 11·062 (3) | 62·89 | (1, 1) Q. |
| 10·582 (2) | 71·14 | (1, 1) Q. |
| 10·341 (1) | 75·29 | |
| 10·060 (2) | 80·12 | (1, 1) Q. |
| 09·482 (3) | 90·09 | (1, 1) Q. |
| 09·186 (1) | 95·17 | |
| 08·855 (2) | 41500·87 | (1, 1) Q. |
| 08·170 (4) | 12·67 | (1, 1) Q. |

Table VI.—(continued).

| λ (I.A.). | $\nu_{\text{vac.}}$ | Classification and remarks. |
|---|---|---|
| 2408·015 (0) | 15·34 | |
| 07·441 (1) | 25·24 | (1, 1) Q. |
| 06·732 (0) | 37·47 | |
| 06·650 (4) | 38·89 | (1, 1) Q. |
| 05·792 (1) | 53·71 | (1, 1) Q. |
| 05·471 (1) | 59·25 | |
| 04·914 (1) | 68·87 | (1, 1) Q. |
| 04·497 (0) | 76·18 | |
| 03·933 (1) | 85·83 | (1, 1) Q. |
| 02·937 (1) | 41602·98 | |
| 02·848 (1) | 04·61 | |

In concluding, the writer wishes to express his thanks to Prof. A. Fowler for suggesting the investigation and for his continued interest and advice during its course, and also to Dr. W. Jevons for valuable criticism and many helpful suggestions.

### *Summary.*

(1) In addition to the well-known visible (α) band system in the spectrum of MgH two others (β and γ) are found in the ultra-violet spectrum. The β-system is represented by a strong band at λ 2430; while the γ-system covers the range λ 5500 to λ 2430.

(2) The λ 2430 band has been analysed and found to consist of a P, a Q and an R branch, each composed of lines which are apparently single, but are probably doublets resolved only in the region of the band origin.

(3) The rotational analysis shows that the final state for the λ 2430 band is identical with the final $^2S$ state for the 0, 0 band λ 5211 of the α-system, and that the initial state is of the same type as that of the α-system, namely, $^2P$. The α-system is the MgH analogue of the " D " lines of Na, the " comparable atom," while the β-system corresponds to the second member of the $^2P \rightarrow {}^2S$ series of Na, λ 3302·34, 2·94.

(4) The λ 2430 band is the 0, 0 band of the β-system. The Q-heads of other bands of the same system have been detected and measured under low dispersion, and values of the initial and final vibrational quantum numbers $n'$, $n''$ assigned. This analysis also points to the fact that the final state is the same for the β as for the α-system.

# *Measurements of the Amount of Ozone in the Earth's Atmosphere and its Relation to other Geophysical Conditions.—Part* III.

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## § I.—*Introduction.*

The work described below is a continuation of that given in the former papers—Parts I and II.[*] The main object was to study the distribution of ozone in cyclones and anticyclones. This has now been completed as far as seems possible by private research, and most of the instruments have been sent to new stations[†] in distant regions of the globe in order to obtain a general idea of the distribution of ozone over the world. It must be remembered, however, *that the study of the ozone distribution in cyclones and anticyclones* has really been exceedingly meagre. If, when synoptic meteorology began to be studied, the same number of barometric observations had been taken at six stations, they would hardly have led to an accurate knowledge of cyclones and anticyclones! There may be much of great interest that has been entirely missed in this research, but further work must be left to larger organisations, as it was found that the present investigation using only seven stations taxed individual efforts to the uttermost: over 5000 spectra have been measured at Oxford in the course of the routine work. The observations have been made at the same stations as those described in Part II and the instruments are the same as those used before. In the previous papers the amount of ozone was calculated on the assumption that the ozone was near the ground. Evidence has now been obtained that it is situated at an average height of about 40 to 50 km.[‡] In this paper allowance has been made for this. The difference is only appreciable when observations are made with the sun at less than 30° above the horizon and the error in the previously published results is always small.

Unfortunately a slight defect developed in the optical wedge of the instrument at Valentia, making the ozone values rather uncertain. As the making and calibration of a new wedge would have put the instrument out of use most of the summer it was decided to use it in its defective condition. The Valentia values are therefore a little uncertain, but the error is seldom more than 0·01 cm., so that it is only just appreciable when considering the ozone distribution.

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[*] 'Roy. Soc. Proc.,' A, vol. 110, p. 660 (1926), and A, vol. 114, p. 521 (1927).

[†] Viz., Spitzbergen, Egypt, California, S. India and New Zealand.

[‡] Cabannes and Dufay, 'C. R.,' vol. 181, p. 302 (1925); Lambert, Déjardin and Chalonge, 'C. R.,' vol. 183, p. 800 (1926); Götz and Dobson, 'Roy. Soc. Proc.,' A, vol. 120, p. 251 (1928).

### § II.—*Accuracy of Measurements.*

In both previous papers (Parts I and II) we have discussed the accuracy of our observations, and here only describe certain new evidence of their accuracy and reply to criticisms that have been made recently.

(*a*) *Variability of Solar Radiation.*—In calculating the ozone value it is assumed that the ratio of the energies of two adjacent wave-lengths as emitted by the sun is constant. The values of this constant determined at Oxford in 1927 are almost identical with those found in 1926 ; at Arosa the 1926 and 1927 values differ by a very small amount, which could easily be accounted for by the refocussing of the instrument which was done during the winter. Owing to poor weather conditions the constants have not been redetermined at the other stations. The fact that all values observed at Montezuma are so nearly constant shows conclusively that there can be little error from this cause. There is no apparent correlation between the ozone values at Montezuma and Dr. Pettit's figures for the sun's ultra-violet radiation as received outside the atmosphere.

(*b*) *Length of Exposure.*—Several observations were made at Oxford in close succession using very different lengths of exposure. The ozone values deduced were all nearly identical and showed that the lengths of exposure had no effect on the result.

(*c*) *Photographic Plates.*—Throughout the work Ilford Special Rapid plates have been used, but different batches of plates have necessarily been employed. When a change has been made from an old batch to a new one, Dr. Götz has kindly made special duplicate observations in the excellent conditions at Arosa, and the results from the old and new batches have been identical.

(*d*) *Results from Different Wave-lengths.*—In general the ozone values deduced from measurements of different pairs of wave-lengths agree very closely, but occasionally small differences appear, and continue roughly constant for a few days. The amount is never important but the reason for the differences has not been discovered.

(*e*) *Variability of the Ozone from Minute to Minute.*—There is a very close agreement between individual results of observations at different times of the day during settled weather. At Arosa where conditions are very good, the change throughout the day is often less than 0·003 cm. In very disturbed cyclonic conditions there is often a large continuous change between observations and where this exceeds 0·01 cm. the fact is noted in the table.

A study of the results obtained when calibrating the instruments, when several pairs of simultaneous spectrograms were taken in different instruments, indicates that the probable error of one observation is about 0·005 cm. of ozone. It seems that the ozone varies irregularly by 0·010 cm. or more from minute to minute in cyclonic weather, but the probable error of observation is too great to be sure of this.

(*f*) *Effect of Haze.*—Since small particles in the atmosphere scatter light of short wave-length more than that of longer wave-length, a change in the number of these particles will affect the deduced ozone value. This error was discussed in Part I (p. 677). Several criticisms have, however, since been made to the effect that our observed changes of ozone are really largely due to changes in the purity of the atmosphere. Fortunately, it is very easy to show that this is not the case. Haze may be due to particles of all sizes, but since the ozone is deduced from the relative energies of two wave-lengths the greatest error will be caused by very small particles which scatter light in inverse proportion to the fourth power of its wave-length. Large particles which scatter light of all wave-lengths alike will produce no error. Taking the pair of wave-lengths 3232 and 3052 Å., if the haziness is all due to very small particles, the values of the extinction coefficients due to these particles must always be in the ratio of 100 to 126 (inverse fourth power), so that to obtain any large decrease in the intensity of shorter wave-length in relation to that of the longer, there must be a much larger reduction of the intensities of *both* wave-lengths.

Now let us take two days, apparently equally clear, on one of which the calculated ozone value was low, and on the other high. If we can find two photographs, one on each day, having been taken with equal times of exposure and at equal values of sec. Z, we can compare directly the actual energies received in the different wave-lengths. If the calculated increase of ozone on one day is really due to greatly increased haziness we should find *both* the longer and shorter wave-lengths greatly reduced in intensity. As an example consider November 24 and 26, 1926, at Arosa. The data are as follows, where I is the energy received at the surface.

Table I.

| 1926. | Time. | Sec. Z. | Exposure. | Ozone. | Log I. | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 3264. | 3232. | 3052. | 3022. |
| | M.E.Z. | | | | | | | |
| November 24.... | 12 : 28 | 2·66 | 30 sec. | 0·246 | 1·163 | 1·313 | 1·059 | 0·160 |
| ,, 26.... | 12 : 03 | 2·65 | 30 ,, | 0·199 | 1·156 | 1·313 | 1·308 | 0·595 |
| | Difference of values of log I .................. | | | | −0·007 | 0 | +0·249 | +0·435 |

If on November 24 the scattering due to small particles and air molecules were double that on November 26—other conditions remaining the same—we should have observed a value of log I of 0·518 for λ = 3232 Å. and 0·328 for λ = 3052 Å., and even so the calculated ozone would have only risen to 0·232 cm. It is thus obvious that the effect is entirely different from that which would have been produced by an increase in the number of small particles as the energies received in the two long wave-lengths were practically identical and only the short wave-lengths were reduced on the day of much ozone.

Fifteen such pairs of clear days have been selected and the actual energies received have been compared with the result given in the following table.

| — | Wave-length. | | |
|---|---|---|---|
| | 3264 Å. | 3232 Å. | 3052 Å. |
| Mean difference of log I on days of much and little ozone ........................................................ | +0·011 | +0·028 | +0·378 |

It is quite clear from the above that on days when much ozone is observed, only the energy in the shorter wave-lengths—which are strongly absorbed by ozone—is reduced to any appreciable extent, so that the effect cannot be due to haze. The small reduction of the longer wave-length on days of much ozone is due to the fact that even these wave-lengths are slightly absorbed by ozone.

It has been shown in § II (*a*) that there is no appreciable change in the relative energies of the wave-lengths used, as emitted by the sun.

### § III.—*Observed Ozone Values.*

Table II gives the daily ozone values for all our stations in Europe. The values for Montezuma (Chile) are not included as the changes from day to day are so small that it is not possible to be sure of their reality. The Smithsonian Institution's spectrograph was sent to this station in order to see (1) what was the nature of the annual variation in the Tropics, and (2) what changes would occur from day to day at a place where the meteorological conditions remained nearly constant.

The long double journey through the Tropics is definitely harmful to the photographic plates, and the excessive dryness and warmth caused appreciable distortion of the wooden spectrograph. For these reasons one would not place such reliance on the accuracy of the results obtained at Montezuma as on those obtained in Europe. This, however, cannot invalidate the result that the ozone is extraordinarily constant there. There are also signs of a curious small diurnal variation not found at other stations which makes it difficult to assign accurate mean values to each day.

In Table II the amount of ozone is expressed, as usual, as the thickness of an equivalent layer of pure ozone at 0° C. and 760 mm. of mercury, the unit being 0·001 cm.

As was shown previously the variability of the amount of ozone from minute to minute prevents a true mean for the day being obtained from one or two observations, and owing to this and the various errors of observation the daily mean values should not be relied upon to within 0·005 or 0·01 cm.

During 1927 M. Buisson has taken regular observations of the amount of ozone at Marseilles, and kindly supplied us with an advance copy of his results which are now published.* These results show a very close agreement with those obtained for us by Dr. Götz at Arosa. The mean value found by M. Buisson is, however, higher than that at Arosa. This is almost certainly due to the use of somewhat different constants, the wave-lengths employed being also different. The Marseilles values have been inserted on the pressure maps reproduced here, and to make them comparable with the other values they have been reduced so as to make the monthly means at Marseilles equal to those at Arosa.

In the latter part of Table II the average values for the ozone over N.W. Europe are given, as these figures may be useful to others who may wish to compare the ozone values with other phenomena. The area in question is roughly a circle of some 500 miles radius centred on London. Where there are not enough observations to get a very reliable value the figures are marked with a question mark.

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* 'C. R.,' vol. 186, p. 1229 (1928).

Table II (i).—Daily Ozone Values.

Unit = 0·001 cm. of pure ozone at N.T.P.

| Day. | Arosa—Winter, 1926–27. | | | | March, 1927. | | | | April, 1927. | | | | | | Day. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | November. | December. | January. | February. | Oxford. | Valentia. | Lerwick. | Arosa. | Oxford. | Valentia. | Lerwick. | Arosa. | Lindenberg | Abisko. | |
| 1 | 230 | — | 246 | 340 | 352 | 341 | — | 275 | 359 | 314 | 334 | 318 | — | — | 1 |
| 2 | — | — | 236 | 311 | 330 | 342 | — | — | 332 | 357 | — | 328 | — | — | 2 |
| 3 | 223 | — | 229 | 281† | 333 | — | 347 | 317 | 322† | 334 | — | 316 | — | — | 3 |
| 4 | 236 | — | — | 251 | — | — | — | 293 | — | 306 | 307 | 300 | — | — | 4 |
| 5 | 234 | — | — | 286 | — | 330 | 362 | 286 | 294 | — | — | 287 | — | — | 5 |
| 6 | 230 | — | — | — | 350 | — | — | 341 | 319 | — | 290 | 270 | — | — | 6 |
| 7 | 242 | — | 256 | 253† | 384 | 335 | — | 328 | 359 | 367 | — | 272 | — | — | 7 |
| 8 | 231 | — | — | 324 | 329 | 319 | 365 | 318 | 373 | 413?† | — | — | — | — | 8 |
| 9 | — | — | — | 294 | 340 | 347 | 359 | 313 | 407 | 374 | — | 285 | — | — | 9 |
| 10 | 254 | — | — | 284 | 375 | 358† | 377 | — | 417 | 364 | 363 | 307 | — | — | 10 |
| 11 | 257 | — | 251 | 277 | 401 ? | 370 | 376 | 293 ? | 381 | — | — | 317 | — | — | 11 |
| 12 | 250 | — | 240 | 268 | 398 | 337 | 324 | 307 | 319 | — | — | 333 | — | — | 12 |
| 13 | 254 | — | 243 | 307 | 386 ? | 366 | 323 | — | 293 | — | — | — | — | — | 13 |
| 14 | 237 | 247 | 299 | 311 | — | — | 332 | 332 | 292 | — | — | — | — | — | 14 |
| 15 | 215 | 275 | — | 325† | 321† | — | — | — | 339 | 310† | 344† | — | — | — | 15 |
| 16 | 232 | — | — | 311 | 294 | 305 | 324 | 287 | 308 | — | 306 | — | — | — | 16 |
| 17 | 239 | 243 | — | 306 | 311 | — | 293 | 280 | 283 | — | 295 | — | — | — | 17 |
| 18 | — | — | 335 | — | 315 | — | — | 283 | 290 | — | 317 | — | — | — | 18 |
| 19 | 247 | — | 362 | — | 275 | — | — | 307 | 307 | — | — | — | 305 | — | 19 |
| 20 | 247 | 263 | 324 | 292 | 272 | 288 | — | 290 | 285 | 289 | — | — | 319 | — | 20 |
| 21 | — | — | 318 | — | 279 | 305 | — | 267† | 286 | — | — | — | — | — | 21 |
| 22 | — | 312 | — | 255 | 309 | — | — | 263 | 301* | 312 | — | — | — | — | 22 |
| 23 | — | 285 | — | 273 | — | 385 | — | 269 | 319 | 308 | 364 | — | 313* | — | 23 |
| 24 | 259 | 258 | — | 320 | 353 | 360 | — | 352 | 296 | — | 330 | 309 | 322 | — | 24 |
| 25 | 232 | 249 | 320* | 314 | 390 | — | — | 283 | 296 | — | 395 | 293 | 349 | — | 25 |
| 26 | 210 | 260 | 304 | 306 | 378 | 376 | — | 308* | 304 | 285 | — | 290 | 322 | — | 26 |
| 27 | — | 263 | 310 | 293 | 374 | 385 | — | — | 313 | 298 | — | 290 | — | 383 | 27 |
| 28 | — | 264 | 318 | 263 | 381 | — | — | — | 295 | — | — | 305 | — | 366 | 28 |
| 29 | — | — | 275 | — | — | 295 | — | 356 | 312† | 299 | 410* | 300 | 311† | — | 29 |
| 30 | — | — | 303 | — | 330 | 325 | — | — | 305 | 316 | 402 | 302 | — | — | 30 |
| 31 | — | 224 | 333* | — | — | — | 387 | 321 | — | — | — | — | — | — | 31 |

* Ozone value rising through day.

† Ozone value falling through day.

Table II (ii).—Daily Ozone Values.

| Day. | May, 1927. | | | | | | June, 1927. | | | | | | July, 1927. | | | | | | Day. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Oxford. | Valentia. | Lerwick. | Arosa. | Lindenberg | Abisko. | Oxford. | Valentia. | Lerwick. | Arosa. | Lindenberg | Abisko. | Oxford. | Valentia. | Lerwick. | Arosa. | Lindenberg | Abisko. | |
| 1 | 320 | — | 417 | 309 | 323 | — | 313 | 324 | — | 284 | 285 | — | 342 | — | 289 | 282 | 286 | — | 1 |
| 2 | 337† | — | — | 312 | 328 | 377 | 327 | — | — | 270 | 286 | — | 304 | — | 288 | 302 | 306 | 271* | 2 |
| 3 | 312 | — | — | 312 | 334* | 360 | 332* | 341 | 310 | 265 | 285 | — | 289 | — | 286 | 278† | — | 257 | 3 |
| 4 | 321 | 349 | — | 303 | 344 | — | 330 | — | — | 281* | — | — | 268 | — | — | 276 | 286 | 271 | 4 |
| 5 | 333 | 344 | 366* | 305 | 345 | — | — | — | — | 306 | — | — | 327 | 315 | 266 | 272† | 289 | 270 | 5 |
| 6 | 330 | 329 | 330 | 306 | 324 | 398 | — | 305?* | 304 | 297 | 304 | — | 269† | — | 279 | 250 | 279† | — | 6 |
| 7 | 336 | 320 | 312† | 305 | 337* | 357 | 325 | 336 | — | 288 | 334 | — | 300 | 309 | 263 | 254 | 256 | — | 7 |
| 8 | 329† | — | — | 317 | 322 | — | 340 | 318 | — | 274 | 327 | — | 290 | — | 264 | 270 | 269† | — | 8 |
| 9 | 323† | 327 | 321* | 317 | 314 | — | 304* | — | — | 287 | 336 | 298* | 277 | 284 | 263 | 298† | 268 | — | 9 |
| 10 | 282 | 286 | — | 309 | 334* | — | 295 ? | — | — | — | 310* | — | 282 | — | 268 | — | — | — | 10 |
| 11 | 292 | — | — | 321 | 381† | — | 322 | 322 ? | 334 | 278 | 313 | — | 280* | — | 290 | 260 | 261 | — | 11 |
| 12 | 305 | 278 | — | 335† | — | — | 322 | — | 253 | 300 | — | — | — | 293 | 273 | 258 | 270* | — | 12 |
| 13 | 299 | 291 | — | 330 | 378† | — | 323 | 335 ? | 343 | 310 | — | — | — | 300 | 275 | 269 | 270 | — | 13 |
| 14 | 302 | — | 319 | 324 | 367 | 384* | — | — | — | 278 | 294 | 318 ? | — | 307 | — | 287 | 279 | 268 | 14 |
| 15 | 304 | — | — | 315 | — | 367† | 300 | — | 316 | 273 | 296 | — | — | 298 | 273 | 285 | — | 251 | 15 |
| 16 | 306 | 315 | 334 | 306 | 325 | — | 267 | — | — | 268 | 287 | — | — | 299* | 268 | 272 | — | — | 16 |
| 17 | 328 | 299 | 342† | 304 | 320 | 341 | 301* | 318 ? | 281 | 269 | 272 | — | 284 | — | — | 273 | 272 | — | 17 |
| 18 | 301 | 310 | 355 | 301 | 320 | 339 | 298† | — | 310 | — | — | 273 | 285 | 307 | 273 | 286* | — | — | 18 |
| 19 | 324 | 311 | 343 | 279 | 302 | 337 | 308† | — | — | 263 | 282 | — | 279 | — | 276 | 273 | — | — | 19 |
| 20 | 311 | — | — | 287* | 338 | 332 | 269 | — | 318 | 261 | — | — | — | — | 280 | 257 | — | — | 20 |
| 21 | 346 | 324 | — | 296 | 318* | 363* | — | 327 | — | 268 | 310 | — | 302 | 300 | — | 256 | 278 | 283 | 21 |
| 22 | 353 | — | 342 | 326 | 353 | — | 303 | — | — | 255 | 297 ? | — | 308 | — | 271 | 258 | — | 280 | 22 |
| 23 | 318 | 281 | — | 345 | — | — | 320 | — | — | 278 | 302* | — | 282† | 282 | — | 281† | 300* | — | 23 |
| 24 | 279 | 280 | 313 ? | 310 | — | — | — | 296 | 309 | 286† | 311 | 298 | — | — | 289 | 280 | 289 ? | — | 24 |
| 25 | 282 | — | 316 ? | 291 ? | 335* | — | — | — | — | 309 | 331 | 294 | 269 | — | 296† | 258 | — | — | 25 |
| 26 | 300 | 316 | 326 | 284 | 352 ? | 328 | 338 | 317 | 316 | 272 | — | — | 287 | — | 290 | 256 | 285 | — | 26 |
| 27 | — | 290 | 351 | 307 | 353 | — | 332 | — | — | — | — | — | 298 | 324 | — | 254* | — | — | 27 |
| 28 | 356* | 315 | — | 307 | — | — | 322 | 314 | 322 | 312 | 356 | 270 | 292 | — | — | 271 | — | — | 28 |
| 29 | 329† | — | — | 298 | 343 | 327 | 310 | — | 287 | 294 | 328 | 285* | 285 | 300 | — | 278 | 280 | — | 29 |
| 30 | 311 | 324 | 300 | 289 | 308 | 306 | 308* | — | 292 | 279 | 304 | — | 274 | 299 | — | 263 | 283 | — | 30 |
| 31 | 325 | 320 | 330 | 269† | 289 | — | — | — | — | — | — | — | 272 | — | 283 | 261 | 278 | 255 | 31 |

* Ozone value rising through day.

† Ozone value falling through day.

Table II (iii).—Daily Ozone Values.

| Day. | August, 1927. | | | | | | September, 1927. | | | | | | October, 1927. | | | | | | Day. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Oxford. | Valentia. | Lerwick. | Arosa. | Lindenberg | Abisko. | Oxford. | Valentia. | Lerwick. | Arosa. | Lindenberg | Abisko. | Oxford. | Valentia. | Lerwick. | Arosa. | Lindenberg | Abisko. | |
| 1 | — | — | 281 | 248 | 256 | — | — | 291 | — | 223 | 233 | — | — | — | — | 245 | 278 | — | 1 |
| 2 | 277† | — | 292 | 254 | 253 | — | 240 | 247 | 251† | 223 | 230 | 222 | 237 | 252 | — | 224 | — | — | 2 |
| 3 | 270 | — | 266 | 270 | — | — | 235 | 241 | 233 | 229 | 233 | — | 247 | 250 | — | 230 | 257 | — | 3 |
| 4 | 269 | — | — | 250 | 262* | — | — | — | 233 | 231 | — | — | 253† | — | — | 240 | 273* | — | 4 |
| 5 | — | 278* | 270 | 255† | 280 | — | — | — | 231 | — | — | — | 247† | 242 | 237 | 252 | — | — | 5 |
| 6 | 271 | — | 264 | 248 | 260 | — | — | 263 | 239 | 231 | — | — | — | — | — | 255 | — | — | 6 |
| 7 | 266 | — | 245 | 258† | 253 | — | 250 | — | — | 229 | 239 | — | 243 | 241 | — | 257 | — | — | 7 |
| 8 | 269 | 289 | — | 248 | 251* | — | 226 | — | — | 250 | — | — | 238 | 253 | — | 240 | 250 | — | 8 |
| 9 | 272 | — | — | 258 | — | — | 213 | 231 | 244 | 237 | — | 233 | 225 | — | — | 233 | — | — | 9 |
| 10 | 281* | — | — | 242 | 263 | — | 253 | — | 253 | 240 | — | — | 233 | 248 | — | 219 | 215 | — | 10 |
| 11 | 272 | — | — | 236 | 248 | — | 259 | 260 | — | 247 | — | — | 224 | 233 | — | 215 | 226 | — | 11 |
| 12 | 273 | — | — | — | — | — | — | — | 243 | 278 | 262 | — | — | 233 | — | 210 | 237 | — | 12 |
| 13 | 264 | — | — | 260 | 277 | — | — | — | 263 | 268 | — | 266 | — | — | — | 219 | — | — | 13 |
| 14 | 269 | — | — | 253 | — | — | — | — | 256 | 262 | — | — | 245 | — | — | 218 | — | — | 14 |
| 15 | — | — | — | 258 | — | — | — | — | — | 256 | — | — | — | — | — | 221 | — | — | 15 |
| 16 | 290 | 296 | 265 | 296 | — | — | 278 | — | — | 258 | 280 | 239 | 220 | — | — | — | — | — | 16 |
| 17 | 286 | — | 285 | 256 | 284 | — | 287† | 263 | 258 | 271 | — | — | — | — | — | 222† | — | — | 17 |
| 18 | 298* | 318 | 292 | 257† | 282 | — | 263 | — | — | 260 | — | — | 242 | — | 277 | 211 | — | — | 18 |
| 19 | 295 | 303 | 282 | 290 | — | 262 | — | — | 253 | 255 | 286 | — | 234 | — | 280 | 220 | — | — | 19 |
| 20 | — | — | 276 | 258 | — | — | — | — | 269 | 239 | 268 | 228 | 232 | — | — | 224 | — | — | 20 |
| 21 | 281 | — | 281 | 246 | — | — | — | — | 248 | 237 | — | 232 | — | — | 251 | 231 | — | — | 21 |
| 22 | 289 | 306 | 280 | 242* | 271 ? | — | — | — | 255 | 235 | 255 | — | — | 272 | 240 | 228 | — | — | 22 |
| 23 | 281 | 306 | 280 | 243 | 253 | — | — | — | — | 247 | — | — | — | — | — | 261* | — | — | 23 |
| 24 | 294 | 319 | 290 | 239 | 260 | — | — | — | 274 | 245 | — | — | 222 | — | — | 239 | — | — | 24 |
| 25 | 293 | 282 | 279 | 264 | — | — | — | — | — | — | — | — | — | — | — | 223 | — | — | 25 |
| 26 | — | — | — | — | — | 256 | — | — | 280 | 249 | 290 | — | — | — | — | — | — | — | 26 |
| 27 | 251* | — | 257 | 275 | 284 | 260 | — | 279 | 258 | — | 278 | — | — | — | — | 215 | — | — | 27 |
| 28 | — | 283 | 291* | 249 | — | — | — | — | — | 252 | 280 | — | — | — | — | 210 | — | — | 28 |
| 29 | 251 | 284 | 303 | 232 | 242 | 266 | — | — | — | 252 | 292 | 254 | 220 | — | — | 209 | — | — | 29 |
| 30 | 258 | 274 | 289 | 231 | 246 | 265 | — | — | 293 | — | — | — | — | — | — | 205 | — | — | 30 |
| 31 | 244 | 273 | — | 233 | 243 | — | — | — | — | — | — | — | 241 | — | — | 200 | — | — | 31 |

* Ozone value rising through day.

† Ozone value falling through day.

Table II (iv).—Daily Ozone Values—Arosa.

| Day. | 1927. | | 1928. | | | | | | | | | | Day. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | November. | December. | January. | February. | March. | April. | May. | June. | July. | August. | September. | October. | |
| 1 | 209* | 227 | 282 | — | 276 | — | — | 290 | 249 | 237 | 231 | 238 | 1 |
| 2 | 194 | 243 | 267 | — | 274 | — | 277 | 286 | 249 | 228 | 252 | 246 | 2 |
| 3 | 187 | 242 | 242 | 307 | 286 | — | — | 292 | 238* | 220 | 252 | 243 | 3 |
| 4 | 189 | 240 | 265† | — | — | 217 | — | 269 | 232 | 232 | 224 | — | 4 |
| 5 | 214* | 242 | — | 270 | 283 | — | — | 281 | 245 | — | 233 | 212 | 5 |
| 6 | 216 | 253 | — | — | — | 260 | — | 270 | 240 | 258 | 230 | 218 | 6 |
| 7 | 225 | — | 223 | 280 | — | 258 | 305 | 270 | 262 | 246 | 229 | — | 7 |
| 8 | 231 | 265 | 218 | 261 | — | 281 | — | 267 | — | 239 | 235 | 205 | 8 |
| 9 | 231 | — | — | 236† | 288 | 277 | 306 | 247 | 255 | 232 | — | 204 | 9 |
| 10 | 256 | 240 | 246 | 241 | 280 | 268 | 329 | 243 | 255 | 237 | 220 | — | 10 |
| 11 | — | 234 | 250 | 279 | — | 270 | 344 | 283 | 256 | 240 | — | 215 | 11 |
| 12 | — | — | 286 | — | 269 | — | 325 | 266† | 247 | 237 | — | 235 | 12 |
| 13 | — | — | 271 | — | 290 | — | 310 | 250 | 254 | 245 | — | — | 13 |
| 14 | 264 | 220 | 278 | 252 | — | — | 300 | 244 | 248 | 238 | — | — | 14 |
| 15 | 270 | — | 265 | — | — | 261 | 290 | — | 236 | 226 | 238 | 234 | 15 |
| 16 | — | — | — | 235 | 303 | — | 292 | 283 | 250 | — | — | 230 | 16 |
| 17 | 254 | 292 | 257 | 266 | 290 | 309 | — | 307 | 235 | 250 | — | 209 | 17 |
| 18 | 249 | 298 | — | — | 280 | 309 | 280 | 270 | 245 | 242 | 241 | 202 | 18 |
| 19 | — | 268 | — | 262 | 284 | 308 | 279 | 276 | 256 | 246 | 229 | 205 | 19 |
| 20 | — | — | — | 259* | 294 | 318 | — | 288 | 253 | 248 | 223 | 208 | 20 |
| 21 | 257 | 238 | — | 264 | 255 | — | 306 | 278 | 264 | — | — | — | 21 |
| 22 | 255 | — | 265 | 260 | 265 | 307 | 299 | 253 | 253 | 250 | — | — | 22 |
| 23 | — | 247† | — | 253 | 268 | 336 | 302 | 247 | 245 | 240 | — | 230 | 23 |
| 24 | 231 | 230 | 236 | 258 | — | 323 | 309 | 250 | 257 | 240 | 260 | 214 | 24 |
| 25 | 220 | 262† | — | 267 | 262 | 308 | 308 | 245 | 248 | 241 | 253 | 215 | 25 |
| 26 | 208 | 267 | 254 | 263 | — | 296† | — | 251 | 240 | 235 | 243 | 195 | 26 |
| 27 | — | 270 | 275 | 270 | — | 280 | 268 | — | 245 | 233 | 226 | 196 | 27 |
| 28 | 225 | 269 | 313 | 271 | — | 288 | 268 | 262 | 251 | — | — | — | 28 |
| 29 | 236 | 263 | — | 253 | — | 297* | — | 250 | — | 221 | 197 | — | 29 |
| 30 | 240 | 275 | 276 | — | — | 296 | — | 242 | 255 | — | 208 | 213 | 30 |
| 31 | — | 273 | — | — | — | — | — | — | 243 | 241 | — | — | 31 |

* Ozone value rising through day.

† Ozone value falling through day.

Table II (v).—*Daily Ozone Values.*

| Day. | Oxford, 1928. | | | | | | | | Mean values for North-west Europe. | | | | | | | | | | | Day. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Summer, 1926. | | | Spring to autumn, 1927. | | | | | | | | |
| | Mar. | April. | May. | June. | July. | Aug. | Sept. | Oct. | July. | Aug. | Sept. | Mar. | April. | May. | June. | July. | Aug. | Sept. | Oct. | |
| 1 | — | 304 | — | — | 264 | — | 265 | 242 | 285 ? | 265 | 245 | 325 | 330 | 330 | 305 | 305 | 270 | 250 | — | 1 |
| 2 | — | 277 | — | 286 | 262 | — | 267 | — | 270 ? | 265 | 240 | 330 | 330 | 330 | 305 | 300 | 270 | 240 | 245 | 2 |
| 3 | — | — | — | 291 | — | — | 240 | 247 | 255 | 275 | 240 ? | 330 | 325 | 315 | 305 | 290 | 265 | 235 | 250 | 3 |
| 4 | 287 | 317 | 311 | — | 277 | — | 242 | 243 | 260 | 270 | 235 ? | — | 300 | 330 | 310 | 280 | 265 | 235 ? | 255 | 4 |
| 5 | — | 303 | 321 | — | — | — | 253 | — | — | 275 | 240 | 325 | 290 ? | 340 | — | 295 | 270 | — | 250 | 5 |
| 6 | — | 312 | 328 | — | 286 | — | 252 | 240 | — | 285 | 245 | 350 | 300 | 325 | 310 | 275 | 265 | 245 | — | 6 |
| 7 | — | — | 331 | 315 | 270 | — | 227 | — | 270 | 275 | 245 ? | 355 | 335 | 320 | 325 | 275 | 250 | 245 | 245 | 7 |
| 8 | — | 330 | — | 288 | — | — | — | 232 | 265 | — | 240 | 330 | 365 ? | 320 | 315 | 280 | 250 | 240 ? | 245 | 8 |
| 9 | — | 301 | 322 | 310 | 256 | — | — | 238 | 275 | 260 | 235 | 340 | 355 | 320 | 310 | 280 | 260 ? | 230 | 225 ? | 9 |
| 10 | 287 | — | 346 | 323 | 242 | — | 235 | — | — | 275 ? | 235 | 355 | 360 | 315 | 310 | 275 | 265 ? | 250 | 230 | 10 |
| 11 | — | 355 | 344 | 328 | 250 | — | 238 | 225 | — | 275 | 235 | 360 | 350 | 305 | 315 | 275 | 260 ? | 255 | 230 | 11 |
| 12 | — | — | 321 | 308 | 259 | — | 233 | — | 255 | 270 | 245 | 340 | 325 | 330 | 320 | 275 | — | 255 | 225 | 12 |
| 13 | — | — | — | 277 | 250 | — | 246 | — | 255 | 260 | 245 | 345 | 300 ? | 330 | 320 | 280 | 270 ? | 260 ? | — | 13 |
| 14 | 312 | — | 336 | 281 | 242 | — | 235 | — | 260 | 260 ? | 240 | 340 ? | 310 ? | 320 | — | 290 | 270 ? | 260 ? | 245 ? | 14 |
| 15 | — | — | 306† | 308 | 256 | — | 236 | — | 270 ? | 250 | 230 | 320 ? | 320 | 315 ? | 295 | 285 | — | — | — | 15 |
| 16 | — | — | 342 | 307 | 245 | — | 232 | — | 270 ? | 250 | 225 | 300 | 305 ? | 315 | 280 | 280 | 285 | 265 | 225 ? | 16 |
| 17 | — | 330 | — | — | 252 | — | — | — | 265 | 250 | 220 | 295 | 285 ? | 315 | 285 | 280 | 280 | 270 | — | 17 |
| 18 | 315 | 331 | 330 | — | 264 | — | 214 | — | 265 | 255 | 225 | 295 | 295 ? | 315 | 290 | 285 | 290 | 260 | 255 | 18 |
| 19 | — | 364 | — | — | 273 | — | 230 | — | 260 ? | 260 | 225 | 285 | 305 ? | 310 | 295 | 280 | 290 | 265 | 250 | 19 |
| 20 | 270 | 358 | 341 | 303 | 254 | — | 240 | 261 | 265 | 265 | 230 | 280 | 295 | 315 | 290 | 280 ? | 285 ? | 255 | 240 ? | 20 |
| 21 | — | 350 | 325 | — | 262 | — | 245 | 253 | — | 265 | 230 | 290 | 300 ? | 325 | 310 | 280 | 275 | 250 ? | 240 ? | 21 |
| 22 | 281 | 339 | — | — | 260 | — | 247 | — | — | 260 | 230 | 310 | 305 ? | 340 | 295 | 285 | 280 | 250 | 240 ? | 22 |
| 23 | 290 | — | — | 274 | 248 | — | 248 | 211 | 260 | 250 | 240 | 345 | 325 | 315 | 300 | 285 | 270 | — | — | 23 |
| 24 | 287 | 315 | 306 | 268 | 237 | — | — | 225 | 275 | 235 | 245 | 360 | 310 | 300 | 305 | 280 | 280 | 260 ? | 225 ? | 24 |
| 25 | — | 316 | 294 | 258 | 235 | — | 281 | — | 275 | 245 | 250 | 360 | 330 | 305 | — | 280 | 280 | — | — | 25 |
| 26 | 286 | 310 | — | — | — | — | 243 | — | 270 | 255 | — | 360 | 320 | 315 | 310 | 280 | — | 275 | — | 26 |
| 27 | — | 314 | 277 | 298 | — | — | 239 | — | 280 | 255 | — | 350 | 325 | 320 | — | 290 | 265 | 270 | — | 27 |
| 28 | 316 | 322 | 270 | — | 280 | — | — | 243 | 275 | 250 | 255 | 360 ? | 315 | 330 | 325 | 285 ? | 270 | — | — | 28 |
| 29 | — | — | — | 264 | 309 | — | — | — | — | 240 | 245 ? | 330 ? | 325 | 325 | 310 | 285 | 265 | — | 230 ? | 29 |
| 30 | 325 | 307 | 279 | 302 | — | — | 247 | — | 270 | 240 | — | 330 ? | 325 | 305 | 300 | 280 | 260 | — | — | 30 |
| 31 | — | — | — | — | — | — | — | — | 265 | 245 | — | 340 ? | — | 305 | — | 280 | 255 | — | 230 ? | 31 |

* Ozone value rising through day.

† Ozone value falling through day.

*Annual Variations.*—Table III gives the monthly mean ozone values for the different stations. The general character of the annual variation, as given in the previous paper, with a maximum in spring and minimum in autumn, is found for all the European stations. The exact dates of maximum and minimum as found at Oxford and Arosa vary by a month or so in different years. There is a marked difference in the annual variations at different stations, which is presumably due to their different latitudes. In the autumn all stations have roughly equal ozone values, while in the spring the northern stations have much more ozone. These northern stations show a very rapid fall between May and June so that for July, August and September, Abisko and Arosa have almost identical values. This point, which will be referred to again later, is interesting as suggesting that in the Arctic the ozone values are high in spring but relatively low in the late summer.*

Table III.—Monthly Mean Ozone Values.

| Date. | Abisko. | Lerwick. | Linden-berg. | Oxford. | Valentia. | Arosa. | Monte-zuma, Chile. |
|---|---|---|---|---|---|---|---|
| 1926. | | | | | | | |
| July | 251 | 274 | 267 | 267 | — | (253) | — |
| August | — | 268 | 267 | 259 | — | 244 | — |
| September | — | 251 | 245 | 234 | (228) | 230 | — |
| October | — | — | 246 | 245 | (253) | 224 | — |
| November | — | — | — | — | — | 238 | 223 |
| December | — | — | — | — | — | 262 | 218 |
| 1927. | | | | | | | |
| January | — | — | — | — | — | 293 | 212 |
| February | — | — | — | — | — | 293 | 208 |
| March | — | 347 | — | 340 | 341 | 302 | 215 |
| April | (375) | 348 | (318) | 320 | 329 | 301 | 210 |
| May | 355 | 332 | 337 | 319 | 310 | 306 | 209 |
| June | (290) | 285 | 307 | 312 | 320 | 282 | 213 |
| July | 268 | 278 | 279 | 288 | 294 | 272 | 216 |
| August | (262) | 279 | 261 | 275 | 292 | 249 | 224 |
| September | (239) | 254 | 263 | 254 | 259 | 246 | 222 |
| October | — | (257) | (251) | 237 | 247 | 228 | 225 |
| November | — | — | — | — | — | 229 | — |
| December | — | — | — | — | — | 255 | — |
| 1928. | | | | | | | |
| January | — | — | — | — | — | 262 | — |
| February | — | — | — | — | — | 261 | — |
| March | — | | — | 296 | — | 279 | — |
| April | — | — | — | 323 | — | 290 | — |
| May | — | — | — | 317 | — | 301 | — |
| June | — | — | — | 294 | — | 266 | — |
| July | — | — | — | 259 | — | 248 | — |
| August | — | — | — | — | — | 238 | — |
| September | — | — | — | 243 | — | 232 | — |
| October | — | — | — | 238 | — | 216 | — |

---

* Note that the weather of the late summer of 1927 was very abnormal, being wet and stormy in European latitudes about 50° N., but very fine in the extreme north. Further, especially in September, Abisko appears to have been largely in Tropical air which would make the ozone values abnormally low.

At Montezuma the annual variation is only just discernible, but it seems fairly certain that there is a small maximum in the southern spring and minimum in the southern autumn, as might be expected. There seem to be small irregularities about March and August in 1927. It is interesting to note that MM. Cabannes and Dufay, having calculated the amount of ozone from the absorption band in the red and yellow regions, using the Smithsonian Institution's data, found no evidence of an annual variation at Montezuma, while an annual variation was found at California. Their work thus agrees with ours as the small annual variation at Montezuma could hardly have been detected.

## § IV.—*On the Relation between Ozone and Terrestrial Magnetism.*

It has been shown previously that there is a small but definite tendency for days with much ozone to be associated with magnetically disturbed conditions. This relation is again shown in the results for 1927. Table IV shows the average magnetic character on the days of highest and lowest ozone values and *vice versa*. The observations used are those of ozone at Oxford and of terrestrial magnetism at Abinger (Surrey). It was thought that a closer relation might be found by using the mean ozone values for N.W. Europe and the mean magnetic character for several stations in the same region. The results are given in Table V from which it is seen that instead of the relation being closer, as was expected, it is entirely absent. This is a curious result which we cannot explain at present.

Table IV.

| 1927. | Mean magnetic character on days of | | Mean ozone on days of | |
|---|---|---|---|---|
| | Lowest ozone. | Highest ozone. | Lowest character. | Highest character. |
| March | 0·91 | 1·03 | 343 | 332 |
| April | 0·49 | 0·82 | 308 | 330 |
| May | 0·59 | 0·92 | 307 | 322 |
| June | 0·49 | 0·67 | 309 | 316 |

Table V.—Mean Ozone Values on Days of High and Low Magnetic Character (N.W. Europe).

| | 1926. | | | 1927. | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | July. | Aug. | Sept. | Mar. | Apr. | May. | June. | July. | Aug. | Sept. |
| Days of High Character | 267 | 260 | 232 | 324 | 326 | 323 | 305 | 285 | 270 | 252 |
| Days of Low Character | 267 | 258 | 244 | 336 | 316 | 317 | 306 | 281 | 270 | 255 |

### §V.—*Distribution of Ozone in Typical Cyclones and Anticyclones.*

The elucidation of this question was one of the main objects of the present series of ozone measurements, and the broad conclusions are shown in figs. 1 and 2. These maps were constructed by first drawing isobars to represent a typical cyclone and anticyclone, then for each normal cyclone or anticyclone which occurred, the ozone values for each station were entered on the maps in their appropriate positions according to the pressure distribution. To eliminate seasonal variations, differences from the monthly mean ozone values were used.

In general, the results are more regular than might have been expected, and there was little difficulty in drawing lines showing equal ozone values. The region to the north-east of the centre of a cyclone is particularly cloudy, and here the available observations are few so that there is some doubt how the lines should run. Apart from this, there is good evidence of the distribution, though, of course, the figures must not be trusted for small details. The distribution in anticyclones is less definite than that in cyclones.

In the rear of some cyclones there is a strong pressure gradient for northerly winds extending to within the Arctic Circle, and in this case the area of much ozone may extend northwards from the cyclone instead of being chiefly confined to an area in its rear. Another apparently abnormal case is that of an anticyclone situated north of the British Isles and having a strong pressure gradient for northerly winds on its east side. In this case the ozone values are often high even within the area of high pressure on the east and sometimes also on the southern sides of the anticyclone. In such a case there is a very cold current over the area where the ozone is high, from which it follows that the relatively high pressure area at the surface in this region will be converted into a normal or low pressure area in the upper atmosphere.

The distribution of pressure around secondary depressions seems to be

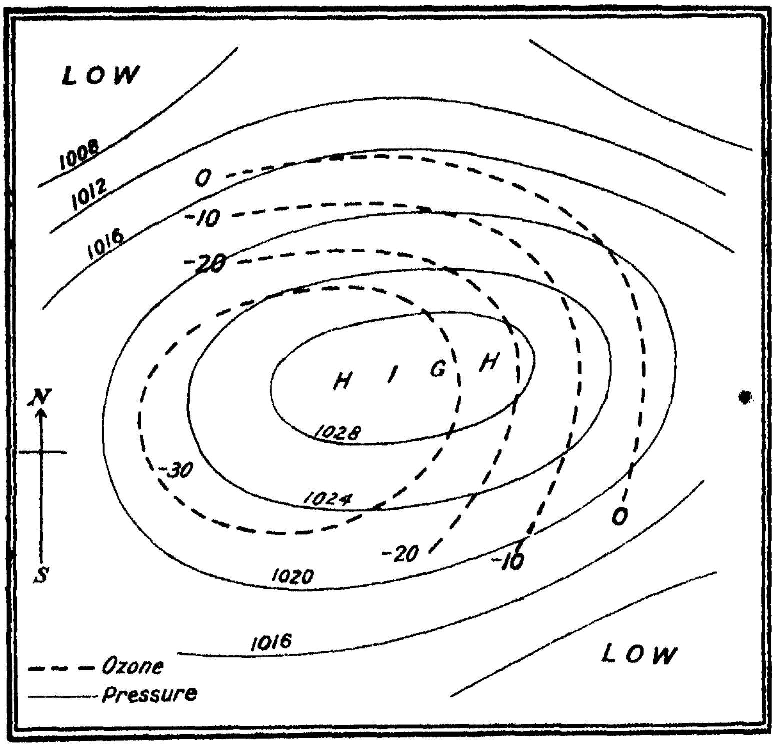
LOW
1008
1012
1016
0
-10
-20
H I G H
1028
-30
1024
-20
-10
0
1020
N
S
1016
LOW
Ozone
Pressure

FIG. 1.

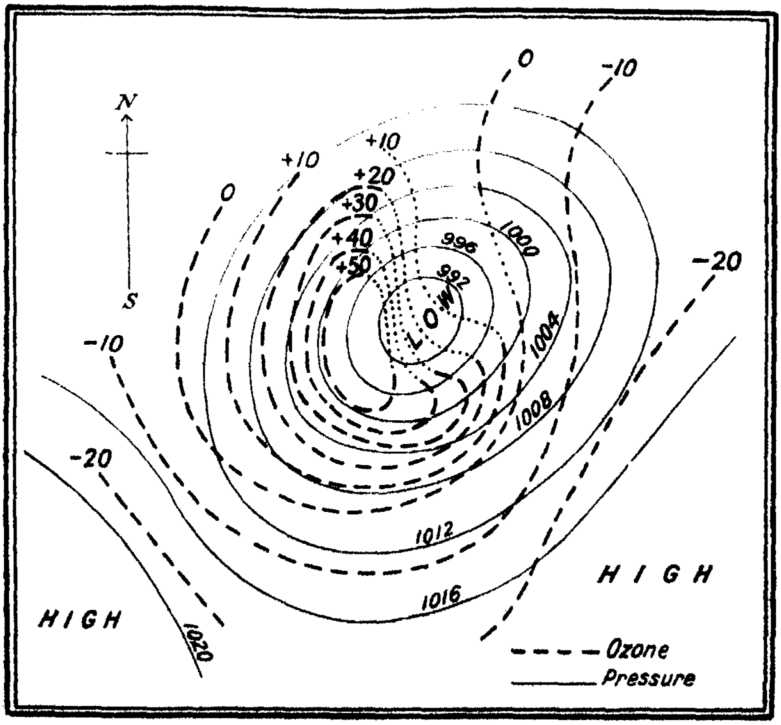
0
-10
N
S
+10
+10
+20
+30
+40
+50
0
996
1000
992
LOW
-20
-10
1004
1008
-20
1012
HIGH
1016
HIGH
1020
Ozone
Pressure

FIG. 2.

similar to that around cyclones, and very high ozone values are sometimes found immediately to the west of secondaries.

Composite maps such as those of figs. 1 and 2 are necessarily subject to the danger of misrepresenting actual facts if, in reality, there are discontinuities. Thus if a map of temperatures of the lower troposphere were constructed in this way, the important feature of the cold and warm fronts would be masked. The small number of ozone observations makes it necessary to use a composite method, and the possibility of real discontinuities must be kept in mind. The evidence is, however, against the existence of discontinuities in the ozone distribution.

It will be seen that the results of the 1927 observations entirely confirm the close connection between the amount of ozone and the pressure distribution which was indicated by the preliminary results obtained in 1926. Figs. 3 to 8* are given to show the changes in the ozone distribution on certain individual occasions for typical pressure distributions. Thus fig. 3 shows the pressure maps at the time when the lowest ozone values ever found were observed. It is noteworthy that the lowest ozone value occurred at Oxford a day before that at Arosa although the high pressure area was spreading westwards, and it is difficult to explain why the ozone should have risen at Oxford on the 3rd while it fell at Arosa.

Fig. 4 shows one of those occasions, when there is a very sudden and local rise in the ozone value at Arosa which seem to be always associated with a small depression, as in this case. Several similar cases have been found, and in some the rise is seen to occur first at Marseilles and a little later at Arosa. The fourth map (May 30) is given to show how uniform the ozone may be over all W. Europe when the pressure is uniform.

Figs. 5 and 6 show the conditions when the highest ozone values were observed during the passage of a cylone across N.W. Europe. April 4 and 6 show the ozone still low in the front of the approaching cyclone : this is marked at Lerwick on the 6th, on which day a small secondary has caused a slight rise at Oxford. A sharp rise occurs at Oxford and Valentia on the 7th with the passing of another secondary, but the greatest rise occurs at Valentia on the 8th, in the rear of a further vigorous secondary (which eventually becomes the

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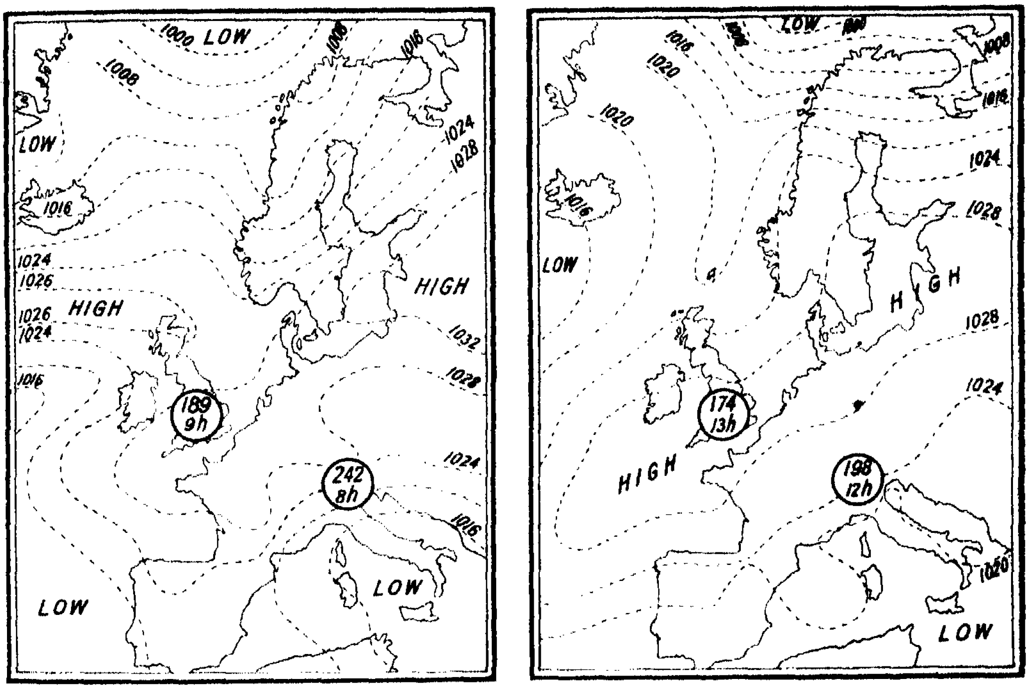
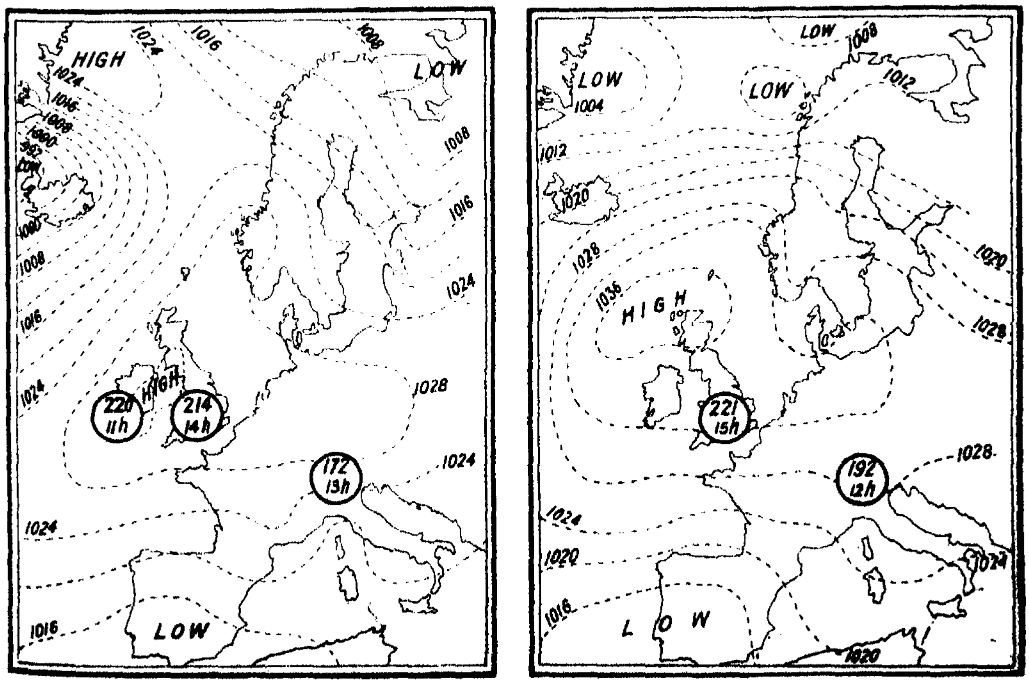
* All the observed ozone values have been plotted on the maps of the Daily Weather Reports in order to study the connection between pressure and ozone changes. It is impossible to give more than a sample of these here, but the original maps could be lent to anyone wishing to make a serious study of them. Such requests should be addressed to us at Boar's Hill, Oxford.

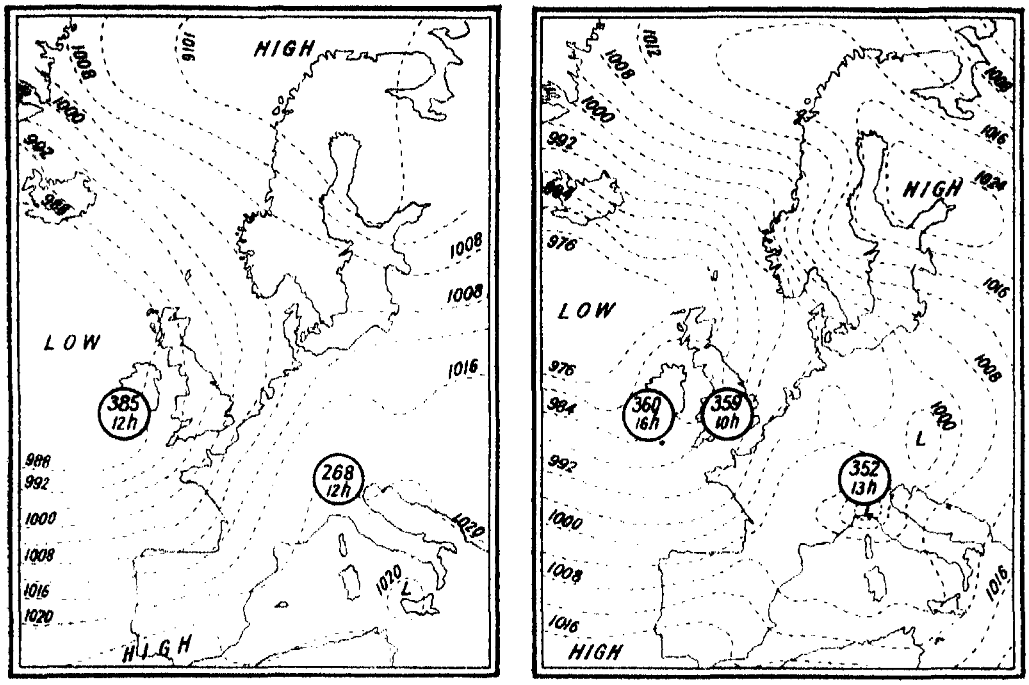


October 1, 1927. 7 A.M. October 2, 1927. 6 P.M.



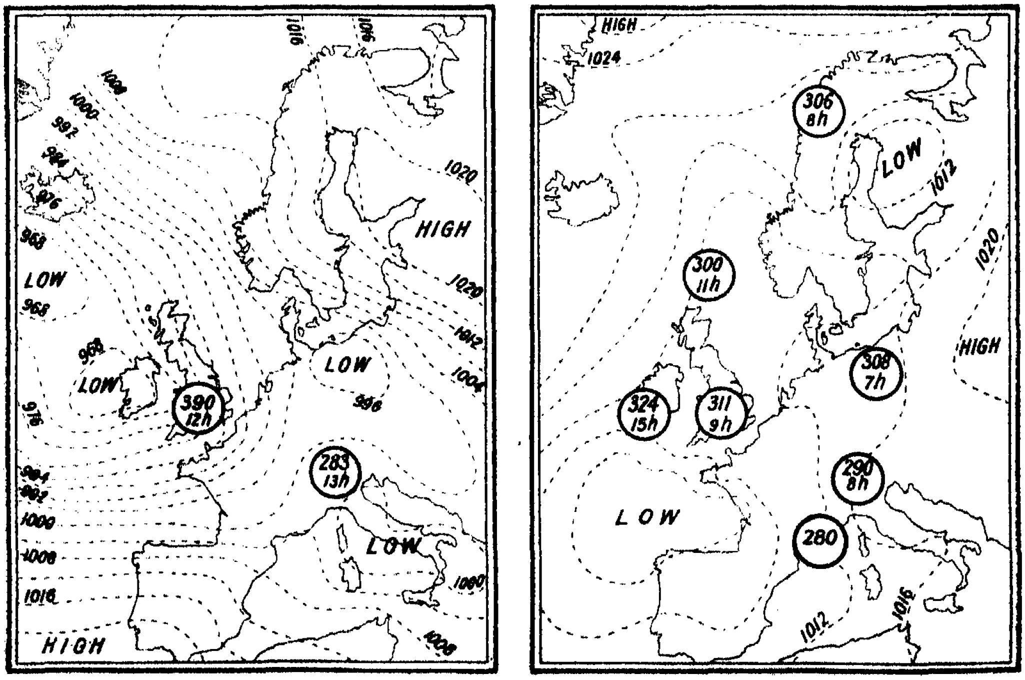
October 3, 1927. 6 P.M. October 4, 1927. 6 P.M.

FIG. 3.



March 23, 1927. 7 A.M.

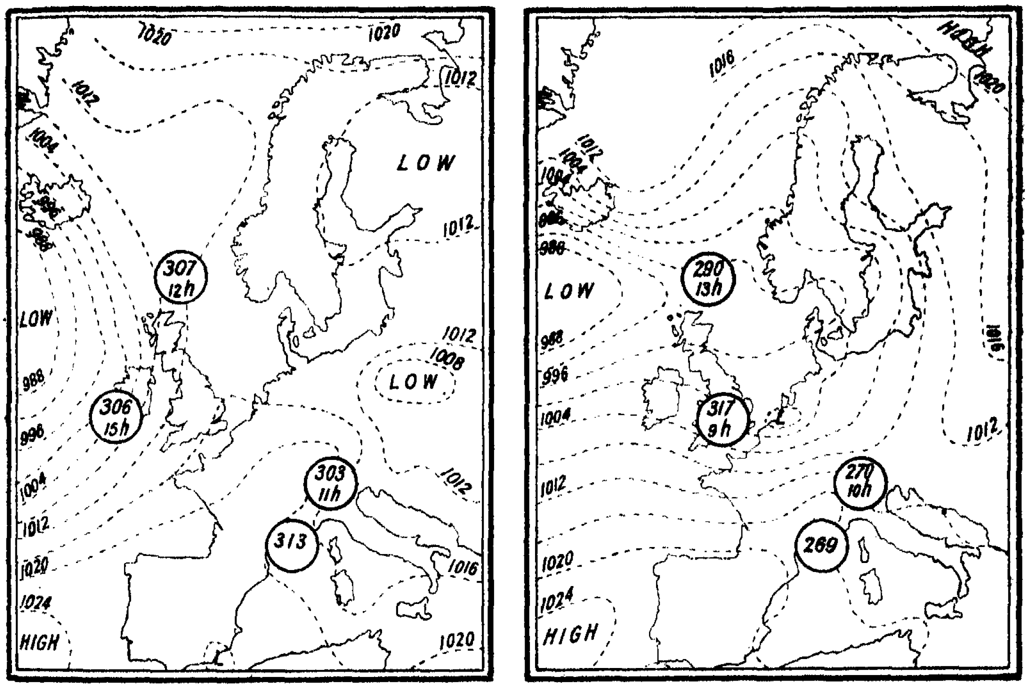
March 24, 1927. 7 A.M.



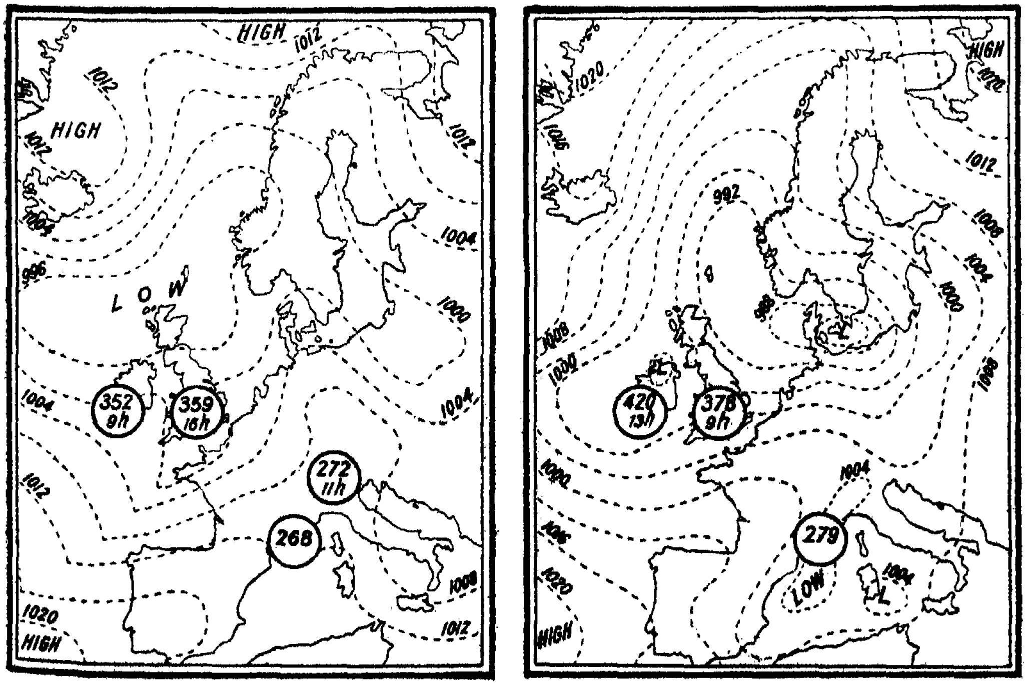
March 25, 1927. 7 A.M.

May 30, 1927. 7 A.M.

FIG. 4.

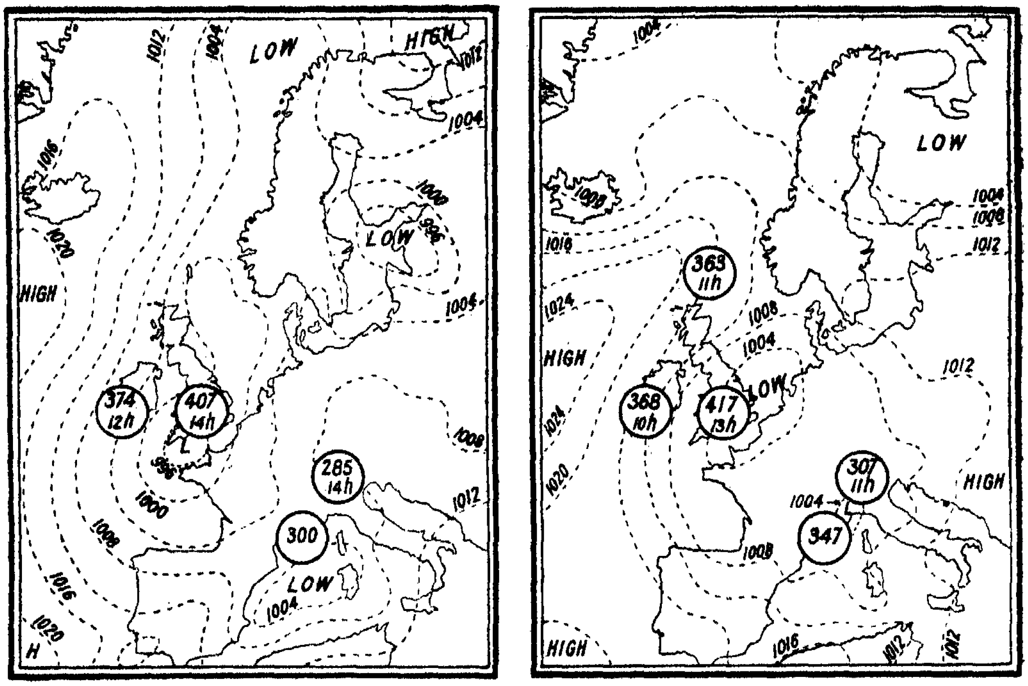


**April 4, 1927.** 7 A.M. **April 6, 1927.** 7 A.M.

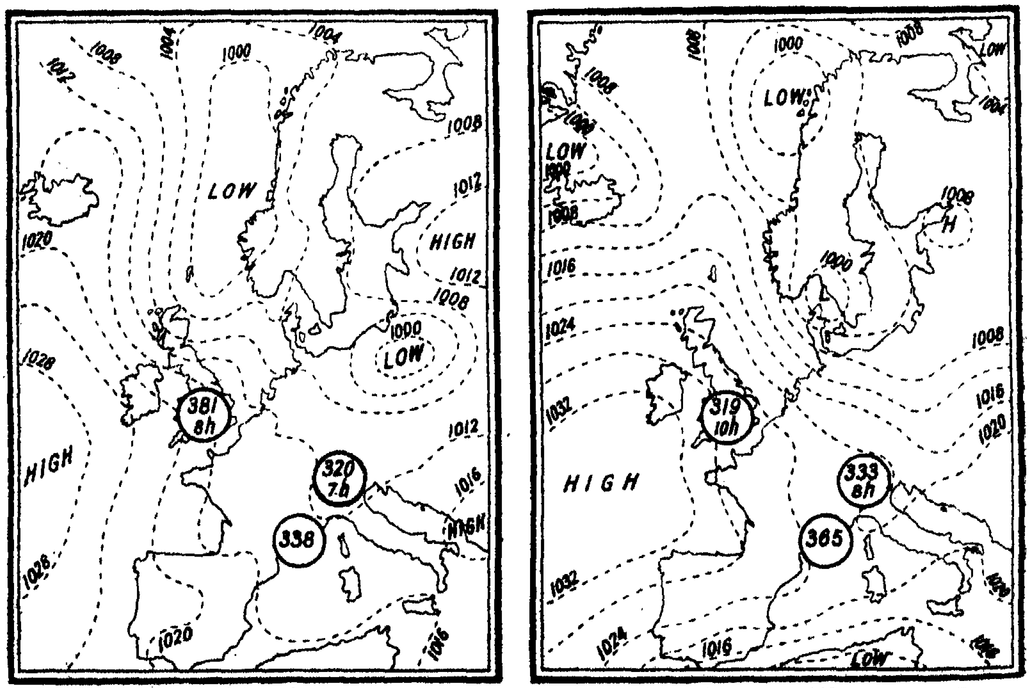


**April 7, 1927.** 7 A.M. **April 8, 1927.** 7 A.M.

Fig. 5.

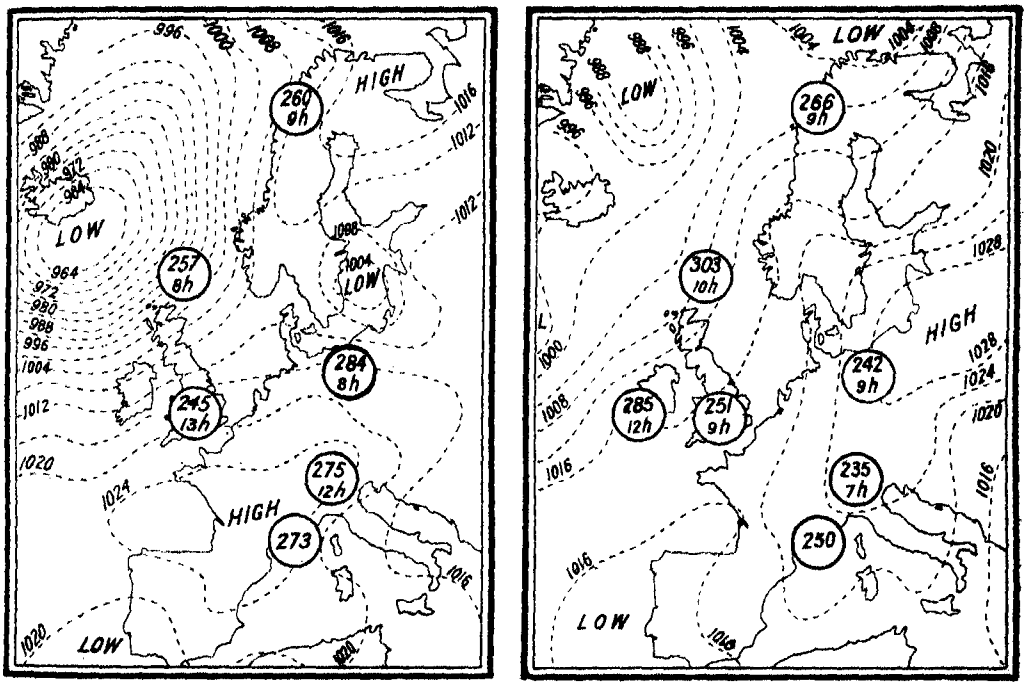


April 9, 1927. 7 A.M.
April 10, 1927. 7 A.M.



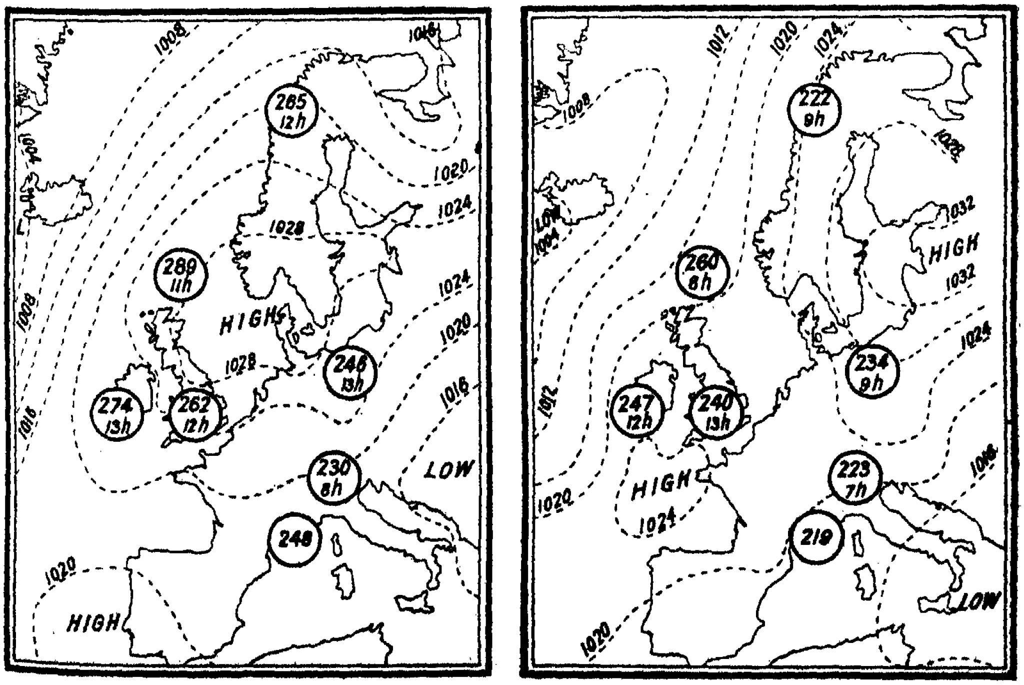
April 11, 1927. 7 A.M.
April 12, 1927. 7 A.M.

Fig. 6.



August 27, 1927. 7 A.M.

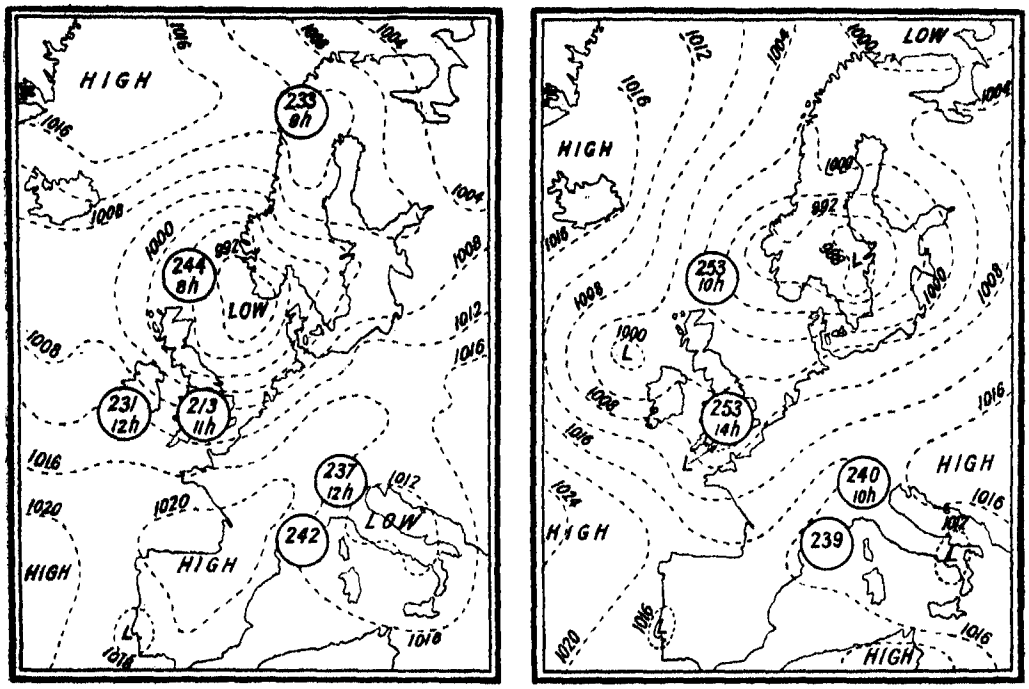
August 29, 1927. 7 A.M.



August 30, 1927. 6 P.M.

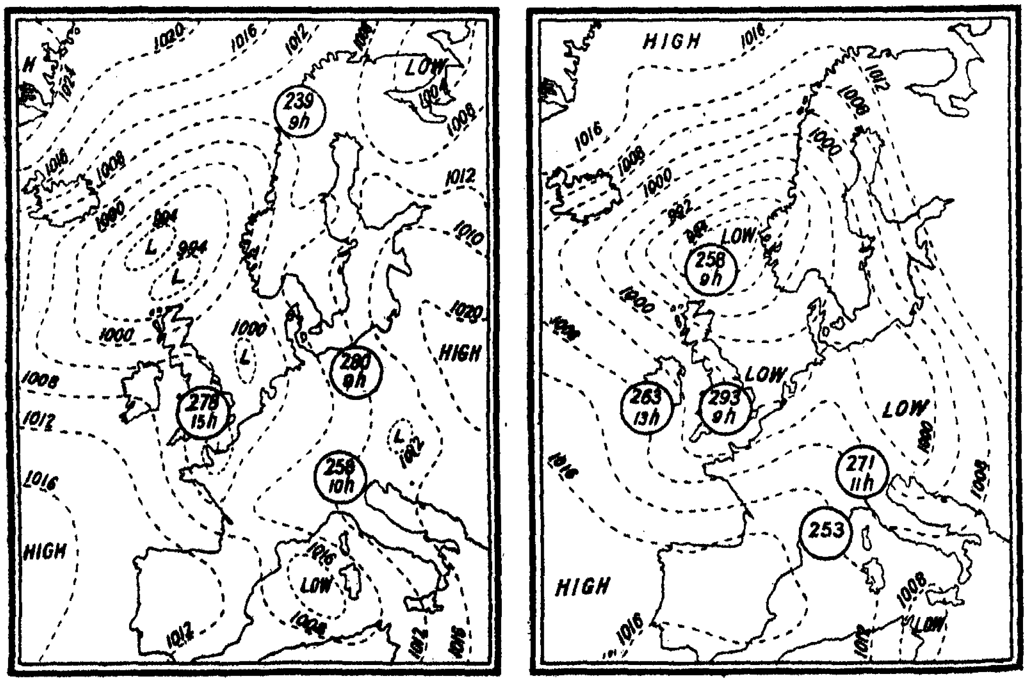
September 2, 1927. 7 A.M.

FIG. 7.



September 9, 1927. 7 A.M.

September 10, 1927. 7 A.M.



September 16, 1927. 7 A.M.

September 17, 1927. 7 A.M.

FIG. 8.

main cyclone), and the area of high ozone travels eastwards with the cyclone. The distribution on April 10, with the highest ozone value at Oxford, would seem to indicate that the maximum ozone occurs in an isolated area in the rear of the cyclone. The fall in the ozone value at Oxford on the 12th with the approach of the anticyclone is very rapid, but Marseilles and Arosa have not yet come under its influence.

Fig. 7 is given to indicate the somewhat variable conditions that may occur in an anticyclone. (The value at Lerwick on the 27th also illustrates the area of low ozone values which is often, but not always, found to the east of a cyclone.) The high values at Marseilles and Arosa on the 27th show that anticyclones do not invariably have low ozone values in all parts. For the remainder, low ozone values are found over all the anticyclonic area except for the higher values at Lerwick and Valentia on the 30th, which are presumably influenced by the cyclone out on the Atlantic.

Finally, fig. 8 shows two apparently very similar cyclones, the first of which is anomalous in that only a very small rise in the ozone value is found in its rear, while the second, a week later, shows a large normal rise. It is disappointing that we are not able to say why there should be such differences. It is possible, but not likely, that the area of much ozone escaped detection on the 9th and 10th ; one would certainly have expected to find high values at Lerwick on these days.

*Variations of Ozone in Polar and Equatorial Air Currents.*—In studying the relation of the ozone variation to the atmospheric conditions, we have also used the weather maps issued by the Norwegian Meteorological Institute at Bergen, which give a diagnosis of the situation each day, indicating the origin and movement of the various air-masses. In what follows, the nomenclature used is that of Bjerknes in his paper on the 'Polar Front Theory of Cyclones.'[*]

It appears very clearly that the origins of the air currents in the upper part of the troposphere have a close connection with the fluctuations of ozone, polar air having a high ozone content and tropical air a low ozone content. This is the more interesting when we remember that the ozone is probably all in the stratosphere, the measurements indicating a height of about 40 to 50 km. for the centre of gravity of the layer[†] (the base of the stratosphere being at a height of roughly 10 km.). The weather maps are based on surface observations, together with cloud observations and a few upper air temperatures obtained from aeroplanes, and the deductions which can be made about the structure of the atmosphere refer mainly to the troposphere. The ozone measurements thus give evidence that the great polar and tropical air currents extend to a great height and bring their own stratosphere with them, if we suppose that they retain their original ozone contents as they travel.

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[*] See Bjerknes and Solberg, "Life cycle of cyclones and the polar front theory of atmospheric circulation," 'Geofys. Pub.,' vol. 3, No. 1 (Kristiania, 1922).

[†] 'Roy Soc. Proc.,' A, vol. 120, p. 251. Note that these height estimates depend entirely on the assumption that there is no regular diurnal variation in the amount of ozone.

We will give now a general qualitative description of the results found. There are anomalies and certain points unexplained, but not more than would be expected, considering the very scanty information available about the conditions in the upper air.

When north-west Europe is covered by " maritime polar " air (that is, air which has arrived *via* Greenland and the Atlantic), the ozone values are about the mean for the time of year, or rather above. A " warm sector," consisting of tropical air, appears over the Atlantic, and the ozone value begins to fall at Valentia and Oxford. This probably indicates the arrival of tropical air at great heights over England, since it is often accompanied by strong westerly winds at the cirrus level and a rise in upper air temperature, while at the surface of the earth the " warm front " is still several hundred miles away. A corresponding fall in the ozone occurs later on at the stations on the Continent. Ozone remains low during the passage of the warm sector, but soon after it has passed the ozone rises rapidly ; the highest values found are those in the rear of depressions, and it is very noticeable that even the smallest secondary depression may cause a large and abrupt rise of ozone. This suggests that at the height of the ozone, the air has come more recently from polar regions than the maritime polar air at the surface.* These high values do not usually persist for long, and by the following day, when the air is described as " maritime polar," the ozone may again be at about its normal value.

This is in agreement with the results previously found, viz., that a depression is associated with a fall in ozone, followed by a sharp rise, and that there is a negative correlation between the amount of ozone and the temperatures up to a height of 8 km.

The surface of separation between tropical and polar air (the " polar front surface ") slopes upward towards the polar side at an angle of about 1 in 100, and it is often found that the ozone value at a station which is in polar air may be very low for some time; in such cases tropical air is always to be found on the weather map at a distance which makes it possible to suppose that at any rate at the top of the troposphere the air over the station is of tropical origin, and this conclusion is usually borne out by upper-air temperatures, when they are available. (Moreover it must be remembered that in taking the photographs the spectrograph is pointed at the sun, whose zenith distance may be as great as 70°; so that, if the height of the ozone is 40 km., the ozone measured may be as much as 110 km. away from the observing station, though as a rule this distance is negligible in the present stage of our investigation.) It is thus often found that the passage of an occlusion coincides with a decrease of ozone, and that when old occluded warm sectors remain stationary for several days, the ozone value may be low even though polar air is apparently well established.

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* Part I, p. 687, end of § VII (*d*) now appears to be incorrect.

Similarly, an outburst of polar air coming southward across Scandinavia does not always bring the high ozone values which one might expect; if a rise is observed, it is only at a considerable distance behind the front of the polar current at the surface, which may reach the Mediterranean without bringing a high ozone value to Valentia or Oxford. In such a case we can suppose that the dense polar air assumes the shape of a comparatively shallow tongue within the warmer air above it.

It was pointed out in Part I (p. 687) that the fall in ozone in an anticyclone showed a lag as compared with the maximum of pressure. We suggest as an explanation of this the theory of the formation of anticyclones put forward by Bjerknes and Solberg in the paper to which we have referred. According to this theory, moving anticyclones are formed between a polar current and a tropical current to the west of it; the earth's rotation gives the northerly polar current a westward tendency and the southerly tropical current an eastward tendency, which result in an area of high pressure between the two. Thus, if the tropical current has a low ozone content, the minimum value of the ozone will tend to be in the westward (*i.e.*, the latter) half of the anticyclone.

*Effect of Pressure Surges.*—While no very well marked case of a general rise or fall of pressure, without much change in the relative distribution, has occurred in N.W. Europe at a time when ozone observations are available, yet it seems clear from such minor cases as have occurred that the effect of surges of pressure on the amount of ozone is almost negligible. In no case is any appreciable connection shown.

*Effect of Föhn Conditions on the Amount of Ozone.*—At our request Dr. Götz, of Arosa, has most kindly made a study of the changes in the amount of ozone there during Föhn conditions. We give below his account of the enquiry *verbatim* :—

> " The connection found by Dobson and Harrison of the increased amount of ozone in the upper layers of the atmosphere with cyclonic conditions was, on the average, fully confirmed by the observations at Arosa with a cadmium cell,* with the exception† that with a typical outburst of Föhn there was an increase in the intensity of the shortest rays of sunlight which were received, indicating a smaller amount of ozone present. In the following study the question has again been taken up using the more accurate data given by the Dobson spectrograph.
>
> " For all the Föhn conditions at Arosa the daily amounts of ozone have been found as a percentage of their respective monthly mean values. The days have been divided into (*a*) the second and first days preceding Föhn conditions ; (*b*) the first, second, and following days with Föhn conditions ; (*c*) the first and second days following Föhn conditions. In the same way the differences of the barometric pressure from its normal ($\Delta b$) in millimetres of Hg were also obtained. Taking the average of ($n$) cases the following results were found :—

" Table VI.

| Days : | Before Föhn. | | Föhn. | | | After Föhn. | |
|---|---|---|---|---|---|---|---|
| | 2 | 1 | 1 | 2 | 3 | 1 | 2 |
| $O_3$ per cent. | 98·3 | 101·7 | 99·0 | 97·6 | 98·8 | 104·0 | 102·4 |
| Mean | 100·0 | | | 98·4 | | 103·2 | |
| $\Delta b$ | 2·2 | 1·3 | —0·3 | —2·1 | —1·2 | —3·2 | —1·5 |
| Mean | 1·7 | | | —1·0 | | —2·3 | |
| ($n$) | (26) | (29) | (30) | (20) | (20) | (24) | (25) |

> " Before and after Föhn conditions the increased ozone is connected with lower pressure but with the drop of pressure at the beginning of Föhn the amount of ozone becomes definitely less.
>
> " The question might be asked to what extent is this anomaly connected with the general pressure distribution over the Continent during Föhn conditions at Arosa (southern Föhn) and to what extent is it caused by the local descending wind at Arosa itself. (For northern Föhn in the South Alps, Suring‡ has found increased atmospheric transparency for ultra-

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* ' Beitr. z. Physik d. freien Atmo.,' vol. 13, p. 19 (1926).

† Götz, ' Das Strahlungs Klime von Arosa,' p. 61 (Berlin, 1926).

‡ ' Met. Z.,' vol. 41, p. 338 (1924).

violet rays with outbursts of Föhn.) Thus, on the suggestion of Dr. Dobson, we have further compared Föhn conditions at Arosa with the same days at Marseilles which never has Föhn. M. Buisson* has published the ozone data for Marseilles and finds a surprising similarity with Arosa, often to the smallest details. The general pressure distribution may be taken as the same both for Marseilles and Arosa.

" Table VII.

| Days : | Before Föhn. | | Föhn. | | | After Föhn. | |
|---|---|---|---|---|---|---|---|
| | 2 | 1 | 1 | 2 | 3 | 1 | 2 |
| $O_3$ per cent. Marseilles | 100 | 100·5 | 99·1 | 99·2 | 98·0 | 103·9 | 101·8 |
| Mean | 100·3 | | | 99 | | 102·9 | |
| $O_3$ per cent. Arosa | 101·4 | 102·1 | 98·5 | 95·8 | 95·2 | 104·8 | 104·0 |
| Mean | 101·8 | | | 97·2 | | 104·4 | |
| $\Delta b$ Arosa | −0·1 | 0·7 | 0·2 | −1·5 | −1·6 | −3·7 | −1·2 |
| Mean | 0·3 | | | −0·8 | | −2·5 | |
| (*n*) | (11) | (12) | (12) | (6) | (4) | (10) | (9) |

" Thus the anomaly is also present at Marseilles which has no Föhn.

" Some typically selected special cases are still more instructive than the mean values and are given in Table VIII."

Table VIII.

| 1927. | Before Föhn. | | Föhn. | | | | | After Föhn. | |
|---|---|---|---|---|---|---|---|---|---|
| Date | April<br>4 | 5 | 6 | 7 | — | — | — | 8 | 9 |
| Ozone—Arosa | 100 | 95 | 90 | 90 | — | — | — | — | 95 |
| Ozone—Marseilles | 101 | 97 | 89 | 89 | — | — | — | 92 | 97 |
| $\Delta b$—Arosa | 3·0 | 2·5 | −0·3 | −2·5 | — | — | — | −5·5 | −5·0 |
| Date | May<br>28 | 29 | 30 | 31 | June<br>1 | 2 | 3 | 4 | 5 |
| Ozone—Arosa | 104 | 101 | 98 | 91 | 97 | 92 | 90 | 96 | 104 |
| Ozone—Marseilles | 102 | 104 | 98 | — | 94 | 97 | 95 | 102 | 104 |
| $\Delta b$—Arosa | 5·4 | 3·1 | 0·0 | −0·1 | −0·7 | 0·6 | 1·8 | −2·0 | −2·0 |
| Date | June<br>28 | 29 | 30 | July<br>1 | — | — | — | 2 | 3 |
| Ozone—Arosa | 113 | 106 | 101 | 102 | — | — | — | 109 | 101 |
| Ozone—Marseilles | 106 | 106 | 100 | 106 | — | — | — | 107 | 107 |
| $\Delta b$—Arosa | −1·3 | −0·8 | −2·3 | −8·1 | — | — | — | −6·1 | −1·3 |

It seems clear from Dr. Götz's study that Föhn conditions, as such, have no influence on the amount of ozone. This is what one would naturally expect seeing that the ozone is at such a great height in the atmosphere. The small fall in the ozone value with decreasing pressure at the beginning of Föhn evidently corresponds to the rather lower ozone values found in the extreme east portion of a cyclone as shown in fig. 2.

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* 'C. R.,' vol. 30, p. 1229 (1928).

*Examination of Special Periods.*—A broad survey of the average relation between the distribution of ozone and the general meteorological situation has been given above, but, as it might be possible to make more progress by examining in detail certain cases which appeared to be of special interest, a number of short periods, where fairly full upper air data were available, have been studied with this end in view. A full discussion of these would take up too much space, particularly as no definite conclusions could be reached which were applicable to all cases. It is clearly shown that the conditions at the surface have little connection with the ozone changes compared with the conditions in the free air. In many cases there seems to be a close agreement between the ozone variations and those of the pressure at, say, 10 km. or with the height of the tropopause, while the temperature in the stratosphere shows but little relation to the changes of ozone content. In other cases the former connection is less marked and the connection with the temperature in the troposphere shows the closest connection with the ozone. On the whole, as previously found, the closest connection is with the pressure at about 10 km. or the average temperature of the troposphere, and as the mutual relation between these two is so close it is not possible to say which is more closely connected with the ozone changes.

*Formation and Travel of Isolated Patches of Large Ozone Content.*—It is of importance to know whether patches with high ozone values can at times be formed over Europe, or whether such isolated patches always drift down from Polar or other regions where the ozone content is permanently high. There are a few cases where such patches with large ozone content seem to have been formed, but with only six stations taking observations (and with many of the observations missing owing to cloudy weather) it is difficult to be sure that these have not drifted over without being shown at other stations on the way.

One of the best examples is that of March 11–13, 1927, when the ozone value at Oxford went up to 400 though the values at Valentia and Lerwick never exceeded 382 within a few days previously. It is possible that this patch of high ozone travelled down from the north-west missing Valentia and Lerwick, but this seems unlikely.

While it is not possible at present to say whether patches of high ozone content may be formed in isolated areas, there are several cases where patches with more ozone than their surroundings have drifted across Europe. On April 8, 1927, air with very high ozone content was observed at Valentia and appeared at Oxford on the 9th and 10th, and presumably had passed eastwards by the 11th. Another case is that of June 26–28, 1927, where a patch with much ozone appeared at Oxford on the 26th and apparently reached Lindenberg on the 28th.

It is noticeable that the air immediately in the rear of a cyclone often has a higher ozone value than that in the same general air stream further to the north or north-west. There seems to be a definite tendency for high ozone values to be closely associated with the western side of a cold front in the rear of a cyclone.

*On the Cause of the Relation between the Amount of Ozone and the Temperature and Pressure in the Troposphere.*—In the two previous reports of this work we have put forward various suggestions regarding the cause of this connection. These all require the average height of the ozone layer to be lower when there is much ozone present. The estimates of the height of the ozone at Arosa show that this is not the case, and therefore these hypotheses cannot be true. It will be seen that the results in the present paper favour the view that the variations are due to the transportation from one region of the globe to another, of large masses of air, including the whole atmosphere up to at least the height of the ozone layer. However, until we know the average amounts of ozone and the height of the layer, in different parts of the world, further speculation is not very profitable. The series of observations now in progress is designed to supply this information, which should be available by the autumn of 1929.

## § VI.—*The Formation and Decomposition of Atmospheric Ozone.*

It has generally been supposed in the past that the ozone present in the upper atmosphere was formed from oxygen under the influence of the sun's ultra-violet radiation of wave-length about 1600 Å., but the results of the present observations make it almost certain that this is not the chief cause of the formation of ozone. We find that the maximum ozone values are associated with air-currents which—at any rate in the troposphere—have recently come from the Arctic, and this is particularly marked in the spring, when the Arctic has been without sunlight for several months. In the same way the smallest ozone values are associated with tropical air-currents in the troposphere. We do not know what the air-currents are at the height of the ozone, but unless we suppose that they are generally in the opposite direction to those in the troposphere, the observations will not support the hypothesis that the ozone is chiefly formed by sunshine. Again, the Abisko and Lerwick observations show very high ozone values in the spring but low values in the autumn, while the results from Chile and our new stations in the Tropics show low ozone values there—probably at all seasons.

It is more in accordance with the observations to suppose that the ozone is formed by some other cause and that the effect of sunlight is mainly to decompose the ozone already present. It is known that while ozone is formed by radiation of wave-length about 1600 Å. it is decomposed by longer wave-lengths. When both wave-lengths are present there will be an equilibrium between these two effects, but it is not possible at present to say what the equilibrium quantity of ozone would be.

The following table shows the times required for ozone to decrease to half its value by the normal thermal decomposition.* The velocity constant of the reaction at the very low concentrations found in the atmosphere may be rather inaccurate, but it is sufficient to show the order of the times required. In calculating the table it is assumed that 3 mm. of pure ozone is contained in a layer of air 10 km. thick, which is probably too high a concentration, making the times too small.

Times for Atmospheric Ozone to fall to Half Value.

| | | | | | |
|---|---|---|---|---|---|
| Temperature .................. | 473° *a* | 423° *a* | 373° *a* | 323° *a* | 273° *a* |
| Time .............................. | 30 hours | 30 days | 4½ years | 730 years | $10^6$ years |

It is clear that the natural decomposition of ozone may be neglected. There may, however, be other reactions causing the decomposition of ozone such as combination with hydrogen, $CH_4$, etc., which may exist in the upper atmosphere.

The only way in which we could reconcile the observed high ozone concentration in the Arctic in spring and the low concentration within the Tropics, with the hypothesis that the ozone is formed by the action of sunlight, would be to suppose a general slow poleward drift in the highest atmosphere with a slow descent of air near the Pole. Such a current would carry ozone formed in low latitudes to the Pole and concentrate it there. If this were the case the ozone at the Poles should be distributed through a moderate depth of atmosphere while that in low latitudes would be all high up. While we have no information about the height of the ozone except in temperate regions, the fact that the average height on days with much ozone appears to be greater than that on days with little ozone indicates that there is not the difference of height that would be expected.

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* See 'Kinetics of Gaseous Reactions,' Hinshelwood.

The fact that the average ozone value found soon after sunrise is nearly equal to that a little before sunset indicates that the decomposition of ozone by sunlight is very slow, the change in one day being hardly detectable. Against this view is the result of M. Chalonge's* preliminary determinations of the amount of ozone at night using moonlight, which indicate a greater amount of ozone by night than by day. If this result is confirmed it will be necessary to suppose that the ozone value drops very rapidly about sunrise to its daytime values, and then remains constant through the day.

The suggestion that the chief effect of sunlight is to reduce the amount of ozone, is in agreement with the rapid fall in the amount of ozone which occurs at Abisko about May. This is the time when the total amount of sunlight received per day in the Arctic is rapidly increasing. (At midsummer the outside of the polar atmosphere receives more solar energy than any other part of the world.) The height of the aurora is from 100 km. up to 500 km. or more, and is certainly much above the average height of the ozone, while the sinking of the ozone through the atmosphere is extremely slow, but Prof. Lindemann has suggested that there may be actions requiring a smaller electric field taking place lower down, whereby ozone is formed.

*Provisional Results of New Observations.*—The following provisional monthly mean values from the new series of observations may be of interest as giving some rough idea of the distribution of the ozone in different parts of the world.

Table IX.

| | Month, 1928. | | |
|---|---|---|---|
| | August. | September. | October. |
| Table Mt., California | 219 | 210 | — |
| Helwan, Egypt | — | (210) | — |
| Kodaikanal, S. India | — | 205 | (203) |
| Christchurch, New Zealand | ... | 298 to 395* | (295 to 355*) |

* Very variable.

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* ‘C. R.,’ vol. 186, p. 1856 (1928).

### *Acknowledgments.*

We have again to thank our many friends for their assistance in this work, without which we should have been quite unable to have accomplished it. As in the previous year the observations have been carried out for us by Dr. F. W. P. Götz at Arosa ; Dr. Duckert at Lindenberg ; Mr. Hogberg at Abisko ; Mr. Lee at Lerwick ; Mr. Stewart at Valentia ; and Mr. Freeman at Montezuma. We are very much indebted to Mr. R. W. M. Gibbs who has measured nearly all the spectrograms and calculated the ozone values, which is a long and tedious work. The Director of the Meterological Office and Mr. Bilham have given us much assistance both in arranging for the British and for some of the foreign observations and in the actual despatch of the instruments, and we have also to thank the Director and Major A. H. R. Goldie for allowing one of us (D.N.H.) to carry out this work in office hours. Prof. Lindemann, F.R.S., and the Clarendon Laboratory have again helped us in many ways. The instruments were the same as those used previously, six of which were obtained by the aid of a grant from the Royal Society and one by a grant from the Smithsonian Institution, who also undertook the observations at Montezuma. The Department of Scientific and Industrial Research has most kindly made us a grant for help with the very large amount of computing work.

# *Some Adsorption Isothermals for a Plane Platinum Surface.*

By WILLIAM GEORGE PALMER, Fellow of St. John's College, Cambridge.

(Communicated by Sir William Pope, F.R.S.—Received October 31, 1928.)

Quantitative experiments to establish the isothermals of adsorption on non-porous surfaces have only rarely been undertaken, owing mainly, no doubt, to the obvious difficulty of measuring the small absolute adsorptions on surfaces of manageable size. Yet it can well be held that many, if not all, of the uncertainties still attaching to the mechanism of adsorption and the constitution of the adsorption layer depend not upon any inherent complexity in the process itself, but upon the complicated geometrical and chemical conditions existing in the accessible surfaces of the porous materials, such as charcoal, that have so often been the subject of study. Moreover, it is by no means easy to determine in many cases what parts of the total "sorption" are due to adsorption, solid solution, or even chemical combination. McBain* has emphasised the sensitiveness of the course of adsorption to the progressive removal of chemical heterogeneity from a porous surface.

Some applications of the electric coherer to adsorption problems have been described in former communications;† it may perhaps be appropriate to recall the main advantages that the method appears to possess over the more direct technique in common use; (*a*) the adsorption takes place on the non-porous and chemically homogeneous surface of a fine metal filament, that can be submitted to heat treatment electrically with great ease; (*b*) there is an immediate and direct test of the "bareness" of the surface, quite independently of the subsequent adsorption experiments; (*c*) from the nature of the technique only true surface films play any part in the measurements. The principal disadvantage is that the adsorbed amount is measured by the critical cohering voltage instead of directly, but this difficulty can be surmounted in the following way.

It has previously been shown‡ that a pure paraffin hydrocarbon of less than 5 carbon atoms in its chain forms on platinum a film so loosely held that the cohering voltage is practically zero. Consider, in the light of the simple theory formerly put forward,* a "dilute" film formed by adsorption from a dilute solution of an adsorbable substance B in such a hydrocarbon. If H is the heat of adsorption per gram-molecule of the substance B

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* 'Nature,' vol. 117, p. 550 (1926).

† 'Roy. Soc. Proc.,' A, vol. 106, p. 55 (1924), vol. 110, p. 133 (1926), and vol. 115, p. 227 (1927).

‡ 'Roy. Soc. Proc.,' A, vol. 115, p. 234 (1927).

$$H = (k - 1)\,E^2A/72 \times 10^4 \times \pi d,$$

where $k$ is the dielectric constant of the film, E the cohering voltage, $2d$ the thickness of the film (in centimetres), and A the area in square centimetres occupied on the surface by a gram-molecule of B. If the film is sufficiently dilute, its dielectric constant will not differ materially from that of the pure hydrocarbon, and H will also be constant while the molecules of B are well separated by the diluent. Hence we may write

$$A = \text{constant}/E^2.$$

$A = N/n$, where N is Avogadro's number, and $n$ the number of adsorbed molecules per unit area. Finally

$$n = \text{constant} \times E^2 \qquad (1)$$

The method so suggested is really equivalent to investigating the adsorption of a gas or vapour at varying pressures, without the troublesome technique of handling the vapour directly. The values of E for saturated films of the substances investigated have already been given,† so that by observing the relations of E in the present work to these maximum possible values it was possible to be certain how far the films could be considered dilute in the sense indicated above.

The coherer used differed only slightly in design from that previously described for use with liquids (*loc. cit.*). The filaments were mounted on platinum leads at both ends (inset, fig. 1), thus rendering them less fragile, and giving an easier means of heating electrically by the two separate connections for each filament. After placing in the coherer, new filaments were first heated at low redness in flowing dry air for some hours, and then in pure dry nitrogen for a further period, the tubes *a* and *b* being used for the gas stream; the mercury trap prevents the gas passing to the left-hand bulb. The heating current was then discontinued, and the filaments tested for a film. It is desirable to clean new filaments in an air current at temperatures not above low redness, rather than in pure oxygen or in air at higher temperatures, to avoid rendering the filaments very fragile and undoubtedly roughening their surfaces, a condition always leading to irregular results afterwards.

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* 'Roy. Soc. Proc.,' A, vol. 106, p. 55 (1926).

† 'Roy. Soc. Proc.,' A, vol. 115, p. 227 (1927).

No lubricant was used in the ground joints *d* and *e*, nor at any other point in the coherer.

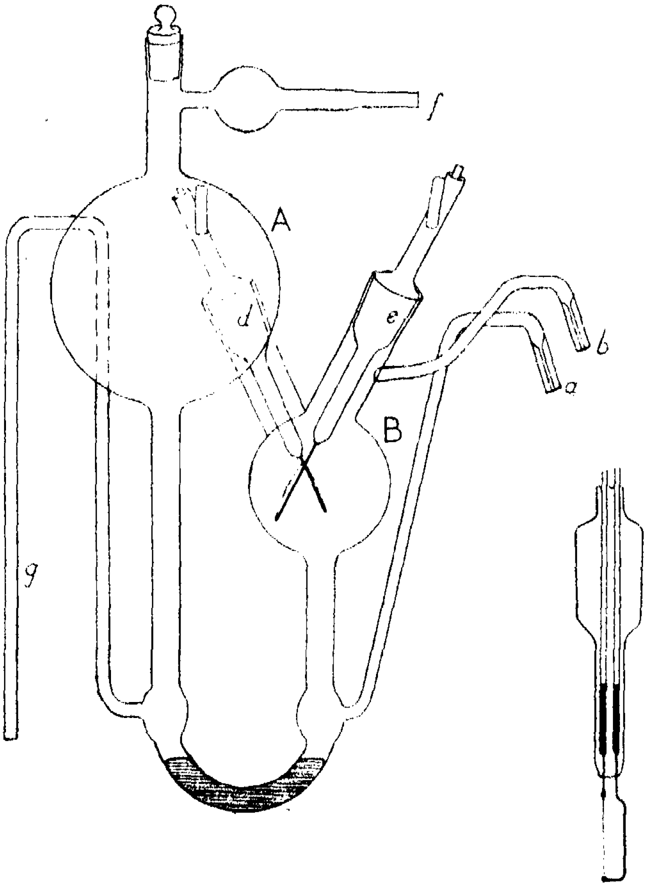

FIG. 1.

The selection of a suitable hydrocarbon to act as diluent at first presented some difficulty. Commercial pure pentane persistently gave a cohering voltage of about 0·5, even after careful drying and re-distillation. A petrol boiling from 40° to 60° was shaken for 2 days with saturated alkaline permanganate solution, washed and dried over sodium wire. A fraction of the product boiling from 40° to 44° (density = 0·640) gave a film only with difficulty, and a cohering voltage not greater than 0·2. The fraction so obtained was used as diluent in all the experiments, and no great difficulty was experienced owing to its volatility. The substances benzene, ethyl alcohol and acetic acid were chosen as adsorptives, as they are chemically representative, and easily obtained pure. Commercial pure benzene was freed from thiophene by boiling with aqueous mercuric acetate,* and finally dried over sodium and frozen out several times. Ethyl alcohol was dried over fresh lime and re-distilled. Acetic acid of the quality used for cryoscopic purposes was purified by freezing.

When the filaments, still in nitrogen, could not be "tapped off," and were therefore clean, 30 c.cs. of the hydrocarbon were poured into the bulb A and forced round into B by attaching the nitrogen supply to *f*. The filaments were then again brought into contact by turning in the joints, and a low voltage confirmed. The electrical arrangements were exactly as described in former work.† A weighed quantity of benzene, or of dilute solutions of alcohol or acetic acid in the hydrocarbon, was now introduced into A from a pyknometer with a long outlet tube. By closing *a* and attaching the nitrogen supply to *b*, the hydrocarbon in B could be forced back into A, and there mixed with the adsorptive by bubbling, and the solution passed back to B. The filaments were thus exposed only to nitrogen during the mixing. The cohering voltage was now obtained, and again half-an-hour later, but in no case was there any change with time, showing that the hydrocarbon was not effectively competing with the adsorptive on the platinum surface. At the close of a series of experiments, the contents of the coherer were withdrawn by means of the side tube *g*, and, after washing out the coherer with small quantities of the hydrocarbon, a fresh supply was placed in B, the filaments not being treated in any further way. In all cases a low voltage was immediately recovered, indicating that no irreversible change had occurred during the experiments.

In the following tables the observed values of $E^2$ are shown in column 2, and the corresponding concentration of adsorptive in the solution in column 1. These concentrations are expressed in millimols (gram-molecules $\times 10^{-3}$) per 100 grams of the hydrocarbon solvent. The degree of association of ethyl alcohol in benzene solution is negligible below concentrations of 0·5 gram per 100 grams of benzene‡; that of acetic acid is negligible below about 0·25 gram per 100 grams of benzene.§ The maximum significant amounts (see Tables II below) contained in a volume of the hydrocarbon equal to that of 100 grams of benzene are found to be 0·103 gram, and 0·090 gram of alcohol and acetic acid respectively. Both of these values are well below the above limits of practical normality in benzene, and it can fairly be assumed that the course of association will be very similar in the two hydrocarbons. Hence in calculating concentrations in the tables, the molecular weights of ethyl alcohol and acetic acid have been taken as 46 and 60 respectively.

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* Dimroth, 'Ber. deutsch. chem. Ges.,' vol. 32, p. 759 (1899).

† 'Roy. Soc. Proc.,' A, vol. 106, p. 55 (1924).

‡ W. E. S. Turner, "Molecular Association," p. 34.

§ Beckmann, 'Z. phys. Chem.,' vol. 92, p. 421 (1917).

Tables I.

*Benzene.*

Pure benzene added to the coherer.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Concentration ......... | 0·6 | 4 | 9 | 18 | 25 | 31 | 45 | 60 |
| $E^2$.............................. | 0·56 | 1·00 | 1·32 | 1·96 | 1·82 | 1·86 | 1·85 | 1·93 |

*Ethyl Alcohol.*

(*a*) Solution added to coherer contained 0·43 gram of alcohol in 16·8 grams of hydrocarbon.

| | | | | | |
|---|---|---|---|---|---|
| Concentration ..................... | 0·32 | 1·02 | 1·45 | 2·00 | 2·55 |
| $E^2$...................................... | 1·24 | 2·32 | 3·25 | 4·00 | 5·20 |

(*b*) Solution added to coherer contained 2·71 grams of alcohol in 21·7 grams of hydrocarbon.

| | | | | |
|---|---|---|---|---|
| Concentration .............................. | 3·55 | 4·60 | 5·90 | 7·25 |
| $E^2$.............................................. | 6·00 | 6·80 | 10·00 | 10·00 |

*Acetic Acid.*

Solution added to coherer contained 0·45 gram of acid in 21·79 grams of hydrocarbon.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Concentration | 0·338 | 0·53 | 0·71 | 0·885 | 1·08 | 1·40 | 1·59 | 1·78 | 2·45 |
| $E^2$................ | 1·44 | 2·25 | 2·90 | 3·60 | 4·40 | 5·62 | 6·35 | 7·05 | 7·62 |

The figures for ethyl alcohol are shown graphically in fig. 2.

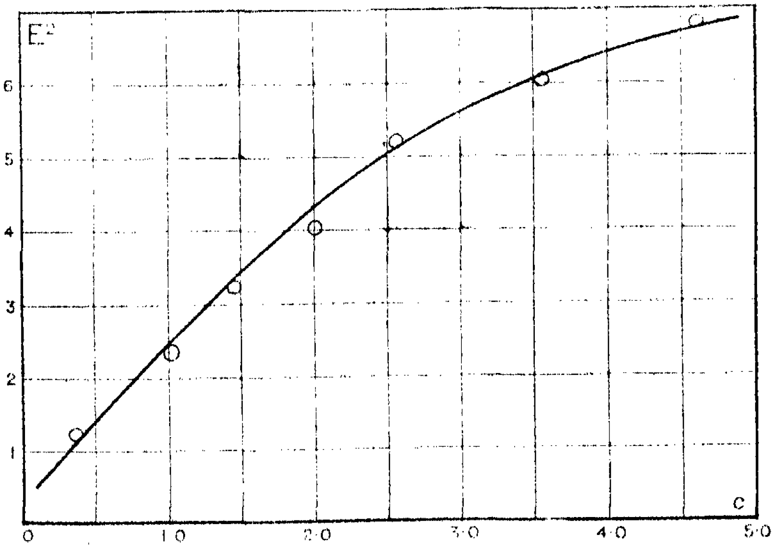

Fig. 2.—Ethyl Alcohol.

For adsorption, either from a gas phase or from solution, on porous materials such as charcoal, the empirical expression

$$a = bc^{1/n} \tag{2}$$

*has been found very generally to represent the relations between the external concentration or pressure c, and the adsorbed amount a, this being usually* calculated for 1 gram of adsorbent. Although $b$ and $n$ remain fairly constant under constant physical conditions, both are functions of the temperature. In the adsorption of gases, $n$ approaches an upper limit with rise of temperature, and it appears that this value remains constant at all temperatures greater than approximately twice the critical temperature of the gas concerned.*

On the other hand, Langmuir has on very simple theoretical grounds proposed a formula

$$a = a_\infty (pc/(1 + pc)), \tag{3}$$

where $a_\infty$ is the amount adsorbed when $c$ is very large, that is the amount at saturation of the surface; and $p$ is a constant representing the average "life" of a molecule of adsorptive in the film.† Unfortunately it appears that this expression has never been tested experimentally under ordinary conditions of temperature and concentration. Such a test is difficult to carry out by direct means, since the above formula applies in its simplest form only to plane surfaces.

Langmuir himself showed that the expression accurately described the adsorption of nitrogen, methane, carbon monoxide, argon and oxygen on plane surfaces of mica at the low pressures 0·00015 — 0·01 cm. of mercury, and at 90° absolute. The expression should also apply to adsorption on plane surfaces from solutions, provided these are dilute so that the adsorption of the solvent remains practically constant. H. von Euler‡ investigated the adsorption of silver ions from an aqueous solution of silver nitrate on a plane gold surface; the following data are read from his adsorption curve:—

| Concentration $c$. (millimols per litre). | $a$. | $c/a$. |
|---|---|---|
| 5·0 | 2·35 | 2·1 |
| 7·5 | 3·35 | 2·25 |
| 10·0 | 4·0 | 2·5 |
| 12·5 | 4·5 | 2·77 |
| 15·0 | 4·75 | 3·15 |
| 17·5 | 4·9 | 3·55 |

If the above values of $c/a$ are plotted against the corresponding values of $c$, an accurately straight line results. Now formula (2) can be rewritten

$$c/a = 1/pa_\infty + c/a_\infty, \tag{4}$$

---

* For discussion, see Freundlich, "Kapillärchemie," p. 150 (1923), *et seq.*

† 'J. Amer. Chem. Soc.,' vol. 38, p. 2221 (1916), vol. 40, p. 1361 (1918).

‡ 'Z. Elektrochemie,' vol. 28, p. 446 (1922).

and hence, when $c/a$ is found to be a linear function of $c$ the expression (2) is proved valid.

## Tables II.

*Acetic Acid.*

| $c$. | $pc/(1+pc)$ $(p = 0{\cdot}15)$. | $E^2_{obs.}$ | $a_\infty/\gamma$ (equation (4)). | $d \log E^2/d \log c$. |
|---|---|---|---|---|
| 0·3 | 0·043 | 1·00 | 23 | 0·72 |
| 0·4 | 0·0565 | 1·70 | 30 | 0·76 |
| 0·5 | 0·070 | 2·05 | 29 | 0·95 |
| 0·8 | 0·107 | 3·24 | 30 | 1·00 |
| 1·0 | 0·130 | 4·00 | 31 | |
| 1·2 | 0·152 | 4·93 | 32 | 0·90 |
| 1·4 | 0·174 | 5·65 | 32·5 | |
| 1·6 | 0·194 | 6·35 | 32 | 0·80 |
| 1·8 | 0·213 | 6·9 | 32·5 | |
| 2·0 | 0·230 | 7·29 | 31 | 0·50 |

*Ethyl Alcohol.*

| $c$. | $pc/(1+pc)$ $(p = 0{\cdot}09)$. | $E^2_{obs.}$ | $a_\infty/\gamma$ (equation (4)). | $d \log E^2/d \log c$. |
|---|---|---|---|---|
| 0·5 | 0·0475 | 1·20 | 25 | 0·50 |
| 1·0 | 0·0910 | 2·10 | 23 | 1·00 |
| 1·5 | 0·130 | 3·25 | 25 | 1·00 |
| 2·0 | 0·167 | 4·24 | 25·5 | 0·85 |
| 3·0 | 0·230 | 5·58 | 24 | 0·55 |
| 4·0 | 0·286 | 6·48 | 23 | |
| 5·0 | 0·334 | 7·00 | 21 | |

*Benzene.*

| $c$. | $pc/(1+pc)$ $(p = 0{\cdot}17)$. | $E^2_{obs.}$ | $a_\infty/\gamma$. (equation (4)). | $d \log E^2/d \log c$. |
|---|---|---|---|---|
| 1·0 | 0·166 | 0·60 | (3·5) | 0·2 |
| 3·0 | 0·375 | 0·85 | 2·25 | 0·35 |
| 5·0 | 0·500 | 1·05 | 2·10 | 0·41 |
| 7·5 | 0·600 | 1·25 | 2·15 | 0·46 |
| 10·0 | 0·660 | 1·40 | 2·12 | 0·50 |
| 12·5 | 0·715 | 1·56 | 2·20 | 0·54 |
| 15·0 | 0·750 | 1·70 | 2·25 | 0·56 |

The graphical relations of $\log c$ and $2 \log E$ for benzene are shown in fig. 3, simple integral values of $c$ being taken on the experimental curve for convenience in this and further calculations. The values of $d \log E^2/d \log c$ obtained from curves by construction are assembled in columns 5 of the above tables. It is at once seen that no exponential expression such as formula (1) can interpret the relations of $c$ and $a$. It is of some interest that the results

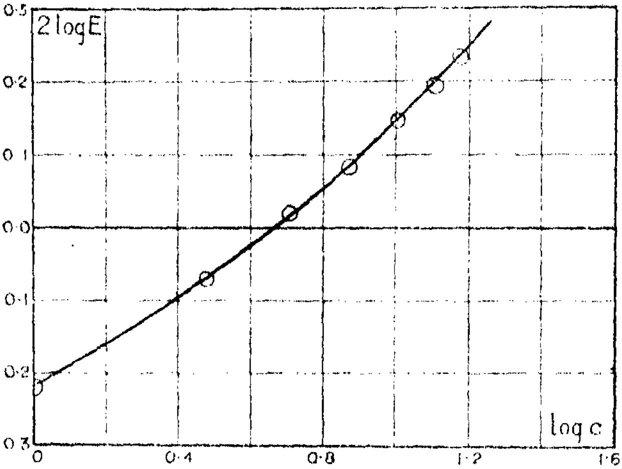

Fig. 3.—Benzene.

of H. H. Lowry and S. O. Morgan* on the adsorption of nitrogen at 0°, and of hydrogen at —192° on the chemically pure porous adsorbent graphite, lead to similar curves for the relation of log $a$ and log $c$, although the variation of the ratio of these quantities is not so wide in this case.

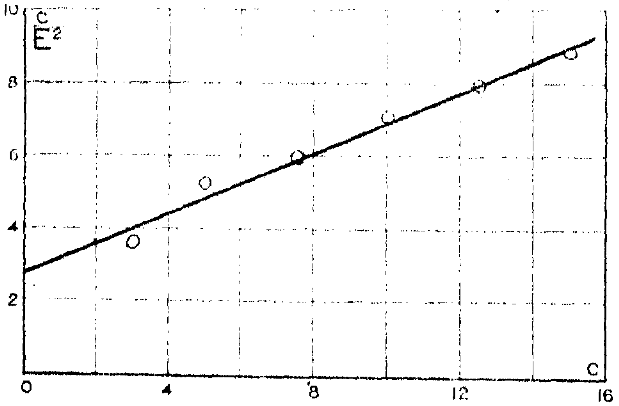

Fig. 4.

Remembering that $E^2$ is proportional to $a$ (equation (1) above) we shall have from Langmuir's formula

$$\gamma E^2 = a_\infty (pc/1 + pc) \tag{5}$$

or

$$c/E^2 = \gamma/pa_\infty + c\gamma/a_\infty \qquad (\gamma \text{ constant}).$$

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* 'J. phys. Chem.,' vol. 29, p. 1105 (1925).

On plotting $c/E^2$ against $c$, straight lines are obtained, of which a specimen (for benzene) is shown in fig. 4. From these lines the following values of $p$ are obtained by determining the ratio slope of line/intercept on $c/E^2$ axis :—

| | Values of $p$ at 20° C. | Critical temperature. |
|---|---|---|
| Ethyl alcohol ........ | 0·09 | 234° |
| Acetic acid .......... | 0·15 | 321° |
| Benzene ............ | 0·18 | 280° |

We may compare these values with those obtained by Langmuir* for gases on mica under the corresponding condition that the "reduced" temperature of the observations is approximately $\frac{1}{2}$.

| | Values of $p$ at $-183°$ C. |
|---|---|
| Methane ............ | 0·10 |
| Nitrogen ............ | 0·08 |
| Oxygen ............ | 0·08 |

In columns 2 of Table II will be found the calculated values of the expression $pc/(1 + pc)$ ; and in columns 3 the figures obtained by dividing this into the corresponding value of $E^2$ ; reference to equation (4) shows that these figures should all equal $a_\infty/\gamma$, a constant quantity for any one adsorptive. It will be seen that the constancy is very satisfactory over a range of external concentration of as much as five or six times. It may, therefore, be concluded that Langmuir's expression is the correct adsorption isothermal for the adsorption of vapours as dilute films on plane surfaces ; and if we take into account von Euler's experiments, it appears that it may also be extended to include the adsorption of ions from aqueous solution.

The similarity in the values of $p$ for the three adsorptives indicates that the "lives" of the adsorbed molecules on the surface are not very different in the three cases. On the other hand, the value of $a_\infty/\gamma$ for benzene is only about one-tenth of its value for the other two adsorptives. Unfortunately, it is not possible to evaluate exactly the constant $\gamma$, which depends principally on the heat of adsorption and the dimensions of the adsorbed molecule (see equation (1) ). The electrical method allows the heat of adsorption to be determined only when the film is complete, as it probably is when the surface is saturated with ethyl alcohol or acetic acid, but the film of benzene is certainly not so, even when the surface is actually immersed in pure liquid benzene.†

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* *Loc. cit. supra.*

† 'Roy. Soc. Proc.,' A, vol. 115, p. 234 (1927).

We may, however, feel reasonably confident that $\gamma$ has the same order of magnitude in all three cases, and thus attribute the difference in $a_\infty/\gamma$ mainly to variation in $a_\infty$. Now $a_\infty$ measures the surface *apparently* available for adsorption, and one explanation of the low value for benzene is that this substance can only be attached to the surface in specialised areas, while practically the whole surface is open to the other adsorptives. While such specialised areas are easily pictured on a porous surface, and have been recently much discussed,[*] Maxted,[†] in an extended and detailed investigation of the "poisoning" of finely divided platinum and palladium by a wide range of substances, has demonstrated that the poisoning effect, both in adsorption and in catalysis, is accurately proportional to the amount of poison added, thus definitely disproving the existence of selective areas on these materials. In any case, the existence of such areas on the annealed surface of a metal must, on general grounds, be held doubtful.

We may avoid this hypothesis *ad hoc* by adopting the converse view that, while all the surface is available for the adsorption of benzene molecules, only a small fraction of the molecules arriving from the external phase at the surface are in a state to be adsorbed. These will be molecules in a specially active, and electrically "open" state, probably as the result of exceptionally violent intermolecular collisions. These special molecules are, in fact, temporarily polar and resemble the normal molecules of permanently polar substances, such as the alcohols and fatty acids. The adsorption of these temporarily polar molecules abnormally prolongs their activity. The usefulness of this view in its relation to the mechanism of catalysis has already been suggested,[‡] and depends on the obvious fact that a prolongation of the lives of existing active molecules means an increased chance of chemical action, and hence is equivalent to an increase in the number of active molecules of normal life. Once adsorption has occurred, the motion of the parts of the adsorbed molecules and that of the adsorbing molecules or atoms will mutually influence each other, and the chemical result of this mutual influence will be specific for both the adsorptive and the adsorbent or catalyst.

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[*] See, for example, Taylor, 'Roy. Soc. Proc.,' A, vol. 108, p. 105 (1925), and vol. 113, p. 77 (1927).

[†] 'J. Chem. Soc.,' T, p. 1050 (1919); pp. 1280, 1501 (1920); p. 225 (1921); p. 1760 (1922).

[‡] 'Roy. Soc. Proc.,' A, vol. 115, p. 234 (1927).

*Summary.*

(1) The method of the electric coherer has been employed to determine the adsorption isothermals of some typical substances on a plane platinum surface.

(2) The results confirm Langmuir's formula.

(3) The variation in the apparent area available for the adsorption of different substances is discussed in relation to the mechanism of adsorption and catalytic action.

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# *Studies of Gas-Solid Equilibria.—Part* II. *Pressure-concentration Equilibria between Benzene and* (a) *Ferric Oxide Gel,* (b) *Silica Gel, directly determined under Isothermal Conditions.*

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In Part I of this work* the pressure-temperature equilibria between these same substances were accurately determined in a number of sealed systems of known and unalterable composition; pressure-concentration isothermals *derived* from these measurements indicated that there was a profound difference between the adsorptive processes of the analogous ferric oxide and silica gels.

In this Part of the work the pressure-concentration equilibria of the same systems (using specimens from the same batches of the gels) have been investigated under isothermal conditions and with known concentrations of benzene varying from zero up to saturation. The effects, on known weights of the gels, of the isothermal addition and the isothermal withdrawal of known quantities of benzene have been determined and "ascending" and "descending" pressure-concentration isothermals have been drawn from these direct measurements.

The existence of a profound difference between the adsorptive processes of these two analogous gels, for benzene, has been fully confirmed.

The experimental procedure adopted in this Part of the work may be summarised as follows :—

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* 'Roy. Soc. Proc.,' vol. 117, A, p. 183 (1927).

An accurately known weight (*in vacuo*) of an activated gel was placed in an all-glass, sealed apparatus consisting of four parts :—

(i) *The reaction system*—a tube, containing the gel, attached to an evacuated mercury manometer—which was contained in a vapour bath and maintained at a constant temperature.

(ii) *The calibrated benzene reservoir* for the storage and accurate measurement of the benzene to be added to and withdrawn from the reaction system.

(iii) *The steam-jacketed, mercury-actuated "cut-off"* for opening and closing the connection between the reaction system and the benzene reservoir.

(iv) *The benzene supply system* for distilling pure benzene, *in vacuo*, into the calibrated benzene reservoir, at the appropriate time ; this was only a temporary portion of the apparatus and it was sealed off after use.

The whole apparatus, with the "cut-off" in the open position, was very thoroughly evacuated. The connection between the reaction system and the benzene reservoir was then closed, by means of the "cut-off" and pure benzene distilled into the benzene reservoir. After sealing off the benzene supply system from the benzene reservoir, the latter was surrounded by a water jacket of known temperature and the exact volume of the contained benzene read off ; from the known volume and temperature of the benzene its exact weight could be calculated.

Connection between the benzene reservoir and the reaction system (which was maintained throughout at a chosen constant temperature) was now opened through the steam-jacketed "cut-off" and benzene transferred to the reaction system ; the exact quantity of benzene transferred in such an operation could be determined by closing the "cut-off" and making a reading of the benzene level in the calibrated benzene reservoir.

After sufficient time had elapsed for the reaction system to reach a state of equilibrium, the equilibrium pressure of benzene vapour was read off directly on the attached manometer ; this pressure was corrected to express the true benzene vapour pressure in centimetres of mercury at 0° C.

Successive determined quantities of benzene were similarly added to the reaction system and the corresponding equilibrium pressures of benzene vapour obtained until the gel was saturated, when the pressure in the reaction system was identical with that of pure benzene at the particular temperature.

Equilibrium pressures were thus obtained between a known weight of gel, maintained at a constant temperature, and known (and gradually increasing) weights of benzene. By plotting these equilibrium pressures against the concentrations of benzene (expressed as grams of benzene per gram of gel), an "ascending" pressure-concentration isothermal was obtained.

Known quantities of benzene were then successively withdrawn from the saturated system which was maintained throughout at a constant temperature; points were thus obtained for the plotting of a corresponding "descending" pressure-concentration isothermal.

It was found possible to make direct and accurate determinations of the equilibrium pressures between benzene vapour and a solid adsorbent under strictly isothermal conditions (using different temperatures) and covering the whole range of concentrations possible in such a system. "Ascending" and "descending" isothermals could be constructed from direct measurements and the reversibility of the equilibrium pressures could be satisfactorily investigated.

The apparatus used in the work is shown in fig. 1 and is conveniently described under four headings, as indicated above.

### (i) *The Reaction System.*

An accurately known weight (*in vacuo*) of the activated gel, in the form of fine granules, was placed in a bulb A, of about 12 c.c. capacity, which was sealed to an evacuated mercury manometer B, made from tubing of 5 mm. bore and long enough to register pressures up to 1 atmosphere. This constituted the reaction system which was connected with the rest of the apparatus through a capillary tube C, of 1·5 mm. bore.

This reaction system was contained in a constant temperature vapour bath D, the connecting tube C passing through the bung which closed the open end of the vapour bath; the bung also carried a tube containing mercury in which the bulb of an accurate thermometer $t_1$ was immersed and a condenser E, connecting to a manostat device for maintaining a constant pressure inside the vapour bath.

The constant temperature vapour bath consisted essentially of a closed cylindrical glass vessel D of length 120 cms. and diameter 6 cms. It was screened, along its whole length, by a polished sleeve of sheet aluminium in which slits were cut for the illumination and reading of the manometer. The bath could be maintained at any chosen temperature (within the range 30° C. to 70° C.) throughout its whole length, by the steady boiling, inside it, of pure alcohol at the appropriate constant controlled pressure. The temperature registered by the thermometer $t_1$, at the top of the vapour bath, was identical with that shown by a second thermometer $t_2$ attached to the gel tube; and this temperature could be maintained constant to one-twentieth of a degree.

The details of (1) the construction and working of the constant temperature vapour bath; (2) the experimental procedure for obtaining an accurately known weight (*in vacuo*) of an activated gel; and (3) the construction of a reliable evacuated mercury manometer, are fully described in Part I (*loc. cit.*) and need not be repeated here.

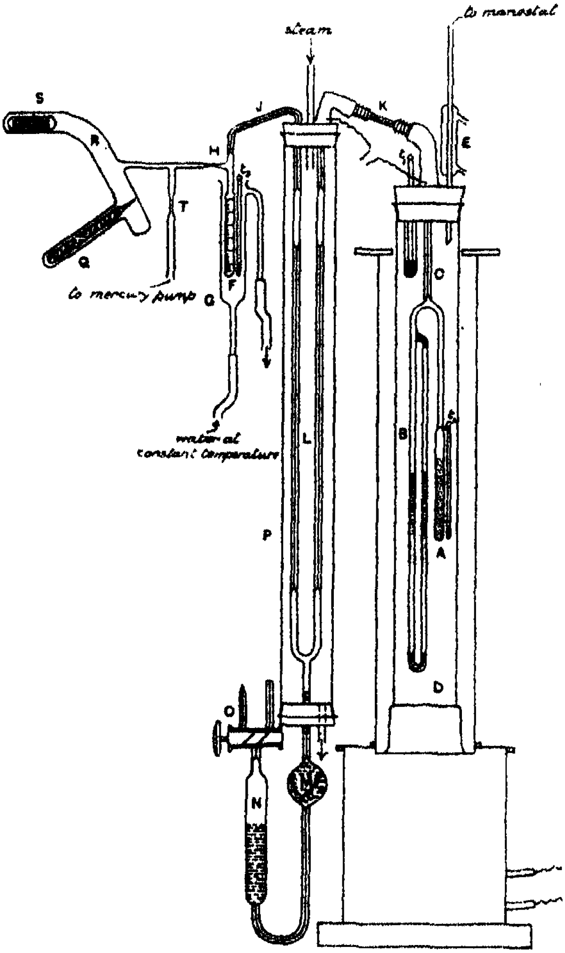


Fig. 1.

### (ii) *The Calibrated Benzene Reservoir.*

This consisted of a graduated tube F, which was carefully calibrated by the weighed mercury method and which could be read, by means of a cathetometer (with scale in the eyepiece), to 0·0025 c.c.

After benzene had been distilled into this reservoir (see later), it was surrounded by a glass jacket G, through which water, at a constant temperature, was made to flow for some time before a reading was taken; the accurate thermometer $t_3$, attached to the reservoir, served to check this temperature. From the known volume and temperature of the benzene contained in the reservoir, the exact weight could be determined at any time.

The benzene reservoir F, was connected, by means of a capillary tube J (of bore 1·5 mm.) to the "cut-off" and thence to the reaction system. It was filled with pure benzene, at the appropriate time, by distillation (*in vacuo*) through the constricted side-tube H, which was then sealed off close to the reservoir.

### (iii) *The Steam-jacketed Mercury-actuated "Cut-off."*

The provision of a satisfactory connecting link—capable of being easily and effectively opened and closed—between the benzene reservoir and the reaction system, was essential to the success of the experiments. Stopcocks were obviously inadmissible and, after many trials, a steam-jacketed, mercury-actuated "cut-off" was devised to meet the peculiar requirements of the case.

The "cut-off" was essentially a long-limbed U-tube (of length 120 cm.) made from capillary tubing of the same bore as the tubes J and K, which connected it with the benzene reservoir and the reaction system respectively. Sealed in at the bottom was a shorter tube connecting it, through the bulb M with a mercury reservoir N, which was closed from the air by a three-way stopcock O. The internal diameter of the "cut-off" was widened to 5 mm. at the U-bend and also near the top of the two long limbs, as shown in the figure.

Connection between the benzene reservoir and the reaction system was closed by pushing the mercury from N into the long limbs of the "cut-off" and opened by withdrawing the mercury to a position below the U-bend; these operations were carried out by the compression and rarefaction, respectively, of the air enclosed above the mercury in N. In closing the "cut-off" the mercury was always brought to the same level in the arm next to the reaction system.

In order to prevent the possibility of benzene condensing at any point in the connecting link between the benzene reservoir and the reaction system it was necessary to maintain the whole of it at a temperature higher than the boiling point of benzene. The "cut-off" was surrounded by a wide tube P, through which steam was blown during the whole course of an experiment. The short lengths of capillary tubing J and K, connecting the limbs of the "cut-off" with the benzene reservoir and the reaction system, were heated electrically; they were covered with asbestos and wound with resistance wire (as shown for one of them, K, in the figure) through which the main current was passed in series with a rheostat.

In the early trial experiments, the "cut-off" was made entirely of capillary tubing, but difficulties were experienced owing to small drops of mercury separating from the main column during the introduction and withdrawal of mercury. This difficulty was successfully overcome by widening parts of the "cut-off" as mentioned above, and by temporarily adjusting the temperature of the benzene reservoir, before opening the "cut-off," so that the pressures in the reservoir and the reaction system did not differ by more than 2 cms.

This "cut-off" constituted a very successful connecting link between the calibrated benzene reservoir and the reaction system. When closed, it effectively sealed the connection between them and, when open, it allowed of the ready passage of benzene vapour from one to the other in either direction. It was effectively sealed from the air and could not therefore introduce any impurity into the system. Since the whole of it was maintained at a temperature higher than the boiling point of benzene, condensation of benzene was prevented at any point between the benzene reservoir and the reaction system. The closing and opening of the connecting link could be carried out smoothly and easily at any time required.

### (iv) *The Benzene Supply System.*

Provision had to be made for the thorough evacuation of the apparatus and, after closing the connection between the reaction system and the calibrated benzene reservoir, for the filling of the latter with pure benzene. This operation involved the distillation of benzene, *in vacuo*, from a supply system attached to the benzene reservoir and capable of being sealed off from it after use. The benzene supply system is shown connected with the benzene reservoir by means of the constricted side-tube H; the figure also shows how the whole sealed apparatus is connected with the mercury pump, drying tubes, etc. through the constricted tube T.

The sealed tube Q, with capillary point on which a fine scratch was made, contained pure benzene (*in vacuo*); it rested in a closed limb of a wide tube R, as shown in the figure. Lying in the horizontal part of R, and capable of being moved by the use of a magnet, was a heavy "bullet" S, made by sealing a soft iron cylinder inside a silica tube.

After the whole apparatus had been thoroughly evacuated and sealed off from the mercury pump at the constriction T, the connection between the reaction system and the benzene reservoir was closed and the capillary point of the sealed tube Q broken off by causing the heavy bullet S to fall upon it. The benzene contained in Q could then be distilled into the benzene reservoir F and the benzene supply system sealed off at the constriction H.

Details of the parification of the benzene and distillation, *in vacuo*, into Q, are given in Part I.

The apparatus shown in the figure, and described above, was sealed to an automatic mercury pump in series with a large drying tube containing pure phosphorus pentoxide and a bulb containing 50 c.c. of highly active nut-shell charcoal granules.

Evacuation was carried out continuously for over 70 hours. During this time the reaction system was maintained at about 130° C. by boiling amyl alcohol in the jacket D surrounding it; steam was blown through the jacket P surrounding the "cut-off" and the mercury contained in the "cut-off" was raised and lowered many times in order to remove from it all traces of dissolved air; the tubes J and K, connecting the "cut-off" to the benzene reservoir and the reaction system, were electrically heated; the bulb containing active charcoal was heated by means of a steam jacket and the benzene reservoir and tubes connecting to the mercury pump were heated, from time to time, by means of a soft blow-pipe flame.

In order finally to "freeze out" any remaining traces of gases from the whole apparatus, the bulb containing active charcoal was allowed to cool and then immersed in liquid air, this cooling being maintained continuously for 48 hours while the rest of the apparatus was heated as described above. The constriction at T was then sealed.

The connection between the reaction system and the benzene reservoir was now closed by raising the mercury in the heated "cut-off" and benzene was distilled from the supply system to the calibrated benzene reservoir F, as described above, after which operation the benzene supply system was sealed off at the constriction H.

The amyl alcohol was carefully washed out from the vapour bath D, surrounding the reaction system, and replaced by pure ethyl alcohol which was made to boil (at a constant, controlled pressure) so as to maintain the reaction system at the constant temperature decided upon ; this temperature was subsequently maintained unaltered during the whole course of an experiment.

The tubes J and K, connecting the benzene reservoir and the reaction system to the "cut-off" were electrically heated and steam was blown through the jacket P surrounding the "cut-off" ; the heating of these parts was maintained throughout the whole subsequent course of an experiment.

The benzene reservoir was surrounded by the constant-temperature water jacket G, and the benzene level read off ; from the known volume and temperature of the benzene, its exact weight was determined.

A sealed glass system was thus obtained comprising (i) a known weight of a gel in a bulb attached to an accurate evacuated mercury manometer—constituting a reaction system maintained at a constant temperature ; (ii) a known weight of pure benzene in an evacuated and calibrated reservoir ; (iii) a device for opening or closing the connection between (i) and (ii) and for transferring benzene vapour from one to the other, in either direction, without the possibility of the benzene vapour undergoing condensation outside (i) or (ii).

When transferring benzene from the calibrated reservoir to the reaction system it was found necessary, for the smooth working of the apparatus, to have the vapour pressure on the reservoir side about 2 cm. higher than that on the side of the reaction system, and *vice versa* when benzene was to be transferred in the opposite direction ; the pressure differences between these two parts could be seen at any moment from the mercury levels in the two limbs of the "cut-off." The temperature of the reaction system could not be altered during the course of an experiment, but the necessary pressure-difference conditions could easily be obtained by a *temporary* adjustment of the temperature of the benzene reservoir. After this operation, the constant-temperature water jacket G was replaced and left for a considerable time before new readings of the benzene level in the reservoir were taken.

Accurately known quantities of benzene could thus be added to or withdrawn from the reaction system under strictly isothermal conditions and by closing the "cut-off" and allowing the reaction system to settle down to a condition of equilibrium, the equilibrium pressure of benzene vapour could be read off after such additions or withdrawals.

It was found possible to obtain equilibrium values up to the point when the gel was saturated at the particular temperature under investigation ; and the reversibility of the system could be examined by a comparison of the "ascending " and " descending " pressure-concentration isothermals thus directly obtained.

(*a*) *The system ferric oxide gel-benzene.*—The weight (*in vacuo*) of ferric oxide gel used was 9·1235 grams. The system was examined at three temperatures—40°, 50° and 60°—and the results are given in Tables A, B and C below. The equilibrium points are numbered in the order in which they were obtained. The benzene content of the gel is given throughout in grams of benzene per gram of gel and the pressures are expressed in centimetres of mercury at 0° C. The results are shown plotted in Graph I.

These isothermals representing the pressure-concentration equilibria between benzene and ferric oxide gel are of the type hitherto found to be associated with systems consisting of dehydrated gels and condensible vapours.

The " ascending " and " descending " isothermals are definitely coincident over the lower ranges of benzene concentration ; they show great divergence (with the production, between them, of a hysteresis region) at intermediate benzene concentrations ; and, finally, they are again coincident over the very steep portions obtained when the benzene concentrations approach the saturation value for the gel. Over the intermediate benzene concentrations the " descending " isothermal is always markedly lower than the " ascending " isothermal. Both " ascending " and " descending " isothermals were shown.

Table A.—Temperature 40° C.

| No. | Concentration of benzene. | Pressure. | No. | Concentration of benzene. | Pressure. |
|---|---|---|---|---|---|
| 1 | 0·0152 | 0·036 | 19 | 0·1261 | 4·988 |
| 2 | 0·0353 | 0·130 | 20 | 0·0988 | 3·652 |
| 3 | 0·0558 | 0·717 | 21 | 0·0731 | 1·770 |
| 4 | 0·0718 | 1·679 | 22 | 0·0955 | 3·429 |
| 5 | 0·0865 | 2·775 | 23 | 0·1373 | 5·954 |
| 6 | 0·1182 | 4·829 | 24 | 0·1819 | 8·041 |
| 7 | 0·1487 | 6·525 | 25 | 0·2096 | 9·699 |
| 8 | 0·1725 | 7·684 | 26 | 0·2269 | 17·373 |
| 9 | 0·1892 | 8·493 | 27 | 0·2246 | 15·025 |
| 10 | 0·2099 | 9·712 | 28 | 0·2165 | 7·098 |
| 11 | 0·2267 | 17·361 | 29 | 0·1804 | 6·171 |
| 12 | 0·2263 | 17·114 | 30 | 0·1596 | 5·842 |
| 13 | 0·2227 | 12·291 | 31 | 0·1361 | 5·456 |
| 14 | 0·2176 | 7·181 | 32 | 0·1108 | 4·447 |
| 15 | 0·2031 | 6·478 | 33 | 0·1053 | 4·106 |
| 16 | 0·1934 | 6·285 | 34 | 0·0902 | 3·078 |
| 17 | 0·1680 | 5·988 | 35 | 0·0678 | 1·457 |
| 18 | 0·1438 | 5·647 | | | |

Nos. 1–11—First " ascending " points. Nos. 12–21—First " descending " points.
Nos. 22–26—Second " ascending " points. Nos. 27–35—Second " descending " points.

Table B.—Temperature 50° C.

| No. | Concentration of benzene. | Pressure. | No. | Concentration of benzene. | Pressure. |
|---|---|---|---|---|---|
| 1 | 0·0421 | 0·401 | 16 | 0·2064 | 10·674 |
| 2 | 0·0621 | 1·787 | 17 | 0·1821 | 9·730 |
| 3 | 0·0907 | 4·954 | 18 | 0·1564 | 9·325 |
| 4 | 0·1106 | 7·080 | 19 | 0·1371 | 8·851 |
| 5 | 0·1295 | 8·720 | 20 | 0·1142 | 7·374 |
| 6 | 0·1514 | 10·441 | 21 | 0·0908 | 4·950 |
| 7 | 0·1642 | 11·379 | 22 | 0·1758 | 12·120 |
| 8 | 0·1790 | 12·421 | 23 | 0·1962 | 13·863 |
| 9 | 0·1961 | 13·737 | 24 | 0·2214 | 19·985 |
| 10 | 0·2025 | 14·469 | 25 | 0·2142 | 12·148 |
| 11 | 0·2162 | 16·598 | 26 | 0·1723 | 9·713 |
| 12 | 0·2219 | 19·795 | 27 | 0·1397 | 9·062 |
| 13 | 0·2250 | 24·305 | 28 | 0·0840 | 4·203 |
| 14 | 0·2331 | 27·079 | 29 | 0·0588 | 1·461 |
| 15 | 0·2207 | 17·959 | | | |

Nos. 1–14—First "ascending" points. Nos. 15–21—First "descending" points.
Nos. 22–24—Second "ascending" points. Nos. 25–29—Second "descending" points.

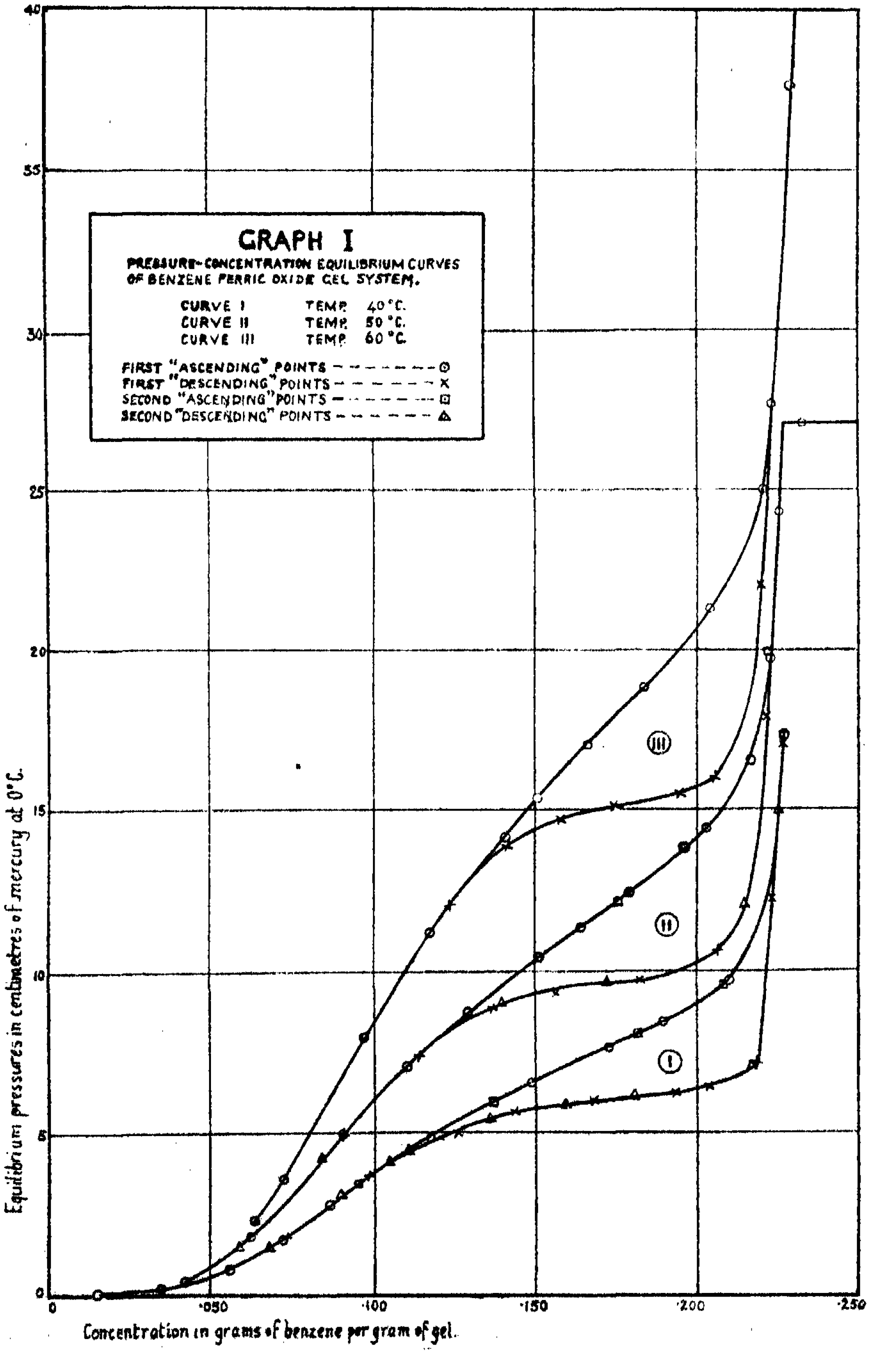
Table C.—Temperature 60° C.

| No. | Concentration of benzene. | Pressure. | No. | Concentration of benzene. | Pressure. |
|---|---|---|---|---|---|
| 1 | 0·0632 | 2·279 | 11 | 0·2230 | 27·694 |
| 2 | 0·0725 | 3·559 | 12 | 0·2289 | 37·603 |
| 3 | 0·0972 | 7·964 | 13 | 0·2196 | 22·072 |
| 4 | 0·1178 | 11·172 | 14 | 0·2050 | 16·007 |
| 5 | 0·1409 | 14·163 | 15 | 0·1946 | 15·537 |
| 6 | 0·1508 | 15·386 | 16 | 0·1749 | 15·163 |
| 7 | 0·1662 | 17·033 | 17 | 0·1584 | 14·720 |
| 8 | 0·1834 | 18·862 | 18 | 0·1412 | 13·843 |
| 9 | 0·2036 | 21·274 | 19 | 0·1241 | 12·100 |
| 10 | 0·2202 | 25·001 | | | |

Nos. 1–12—"Ascending" points. Nos. 13–19—"Descending" points.

at 40° and at 50°, to be definitely repeatable over the whole range of concentrations.

The saturation benzene concentration for the system was reached in the experiment carried out at 50°; and the fact that the pressure obtained (27·079 cm.) lay between the vapour pressure for pure benzene at 50° obtained by Young (26·897 cm.) and that obtained by Regnault (27·137 cm.) affords a proof of the purity of the gaseous phase and the accuracy of the experimental technique employed.


GRAPH I
PRESSURE-CONCENTRATION EQUILIBRIUM CURVES OF BENZENE FERRIC OXIDE GEL SYSTEM.
CURVE I TEMP. 40°C.
CURVE II TEMP. 50°C.
CURVE III TEMP. 60°C.
FIRST "ASCENDING" POINTS ⊙
FIRST "DESCENDING" POINTS ×
SECOND "ASCENDING" POINTS ⊡
SECOND "DESCENDING" POINTS △
Ⓘ
Ⓘⓘ
Ⓘⓘⓘ
40
35
30
25
20
15
10
5
0
0
·050
·100
·150
·200
·250
Equilibrium pressures in centimetres of mercury at 0°C.
Concentration in grams of benzene per gram of gel.

The time taken for equilibrium to be set up was very rapid over the whole range of concentrations when the " ascending " and " descending " isothermals coincided ; pressure became steady after half-an-hour (and thereafter showed no tendency to alter over long periods) whether determined after the addition or after the withdrawal of benzene. Over these intermediate ranges of concentration, when the " ascending " and " descending " isothermals did not coincide, the time taken for equilibrium to be reached was longer, but 2 hours was usually sufficient for the equilibrium pressure to be reached on both the " ascending " and " descending " isothermals.

It is interesting to note that the isothermals *derived* from the pressure temperature curves determined in Part I (*loc. cit.*) correspond to the directly determined *ascending* isothermals.

The results plotted on the " ascending " isothermals in Graph I were obtained after successive additions of known quantities of benzene to the reaction system and those plotted on the " descending " isothermals were obtained after successive withdrawals of known quantities of benzene ; the temperature of the reaction system was maintained strictly at its chosen controlled value throughout the whole of these operations.

Another experiment was carried out at 40° in order to study the effect of interruptions in the smooth addition or the smooth withdrawal of benzene. It was found that if, after an *addition* of benzene and the establishment of equilibrium on the " ascending " isothermal, a known quantity of benzene was *withdrawn*, the new equilibrium point fell exactly on the curve over those ranges of concentration where the " ascending " and " descending " isothermals coincided ; but, over the intermediate range of benzene concentration where the " ascending " and " descending " isothermals did not coincide, a new equilibrium point was obtained and this was always *below* the " ascending " isothermal. Similarly if, after a withdrawal of benzene and the establishment of equilibrium on the " descending " isothermal, a known quantity of benzene was *added*, the new equilibrium point again fell on the curve over the ranges of concentration when the " ascending " and " descending " isothermals coincided ; but, over the intermediate range of benzene concentrations, the new equilibrium point was always *above* the " descending " isothermal.

By these interruptions of the smooth addition or withdrawal of benzene, it was possible to obtain equilibrium pressures within the hysteresis region between the " ascending " and " descending " isothermals. The " ascending " isothermal, obtained by smooth successive additions of benzene to the reaction system, set an upper limit to the equilibrium pressures just as the corresponding " descending " isothermal set a lower limit to the equilibrium pressures.

Further experiments were carried out to study the effect, on an established equilibrium pressure, of temporary alterations in the temperature of the system. The temperature was at one time raised to 78° and at another time reduced to room temperature and left overnight. Next day the system was restored to 40° and maintained at that temperature until equilibrium was attained.

It was found that (1) over those ranges of concentration where the " ascending " and " descending " isothermals coincided, the equilibrium pressure was not affected by temporarily heating or cooling the system and subsequently restoring it to the original temperature; (2) over the intermediate ranges of concentration when the " ascending " and " descending " isothermals did not coincide, the effect of temporary heating or cooling was always to give a new equilibrium point which fell within the hysteresis region between the " ascending " and " descending " isothermal. The limits to the new pressures were again set by the original " ascending " and " descending " isothermals.

It is clear therefore that in the system benzene-ferric oxide gel there are ranges of concentration—a lower and a higher range—over which the pressure-concentration relations are repeatable and reversible; but over intermediate ranges of concentration (the limits of which vary with the temperature) the pressure-concentration relations are not reversible and " ascending " and " descending " isothermals are only repeatable if the system is maintained rigidly at its constant controlled temperature and benzene *smoothly* added to or withdrawn from the system.

It is to be noted that similar results were obtained by one of us (' Roy. Soc. Proc.,' A, vol. 108, p. 456 (1925) ) in the study of the pressure-concentration relationships between palladium and hydrogen.

(*b*) *The system silica gel-benzene.*—The weight (*in vacuo*) of silica gel used was 14·1886 grams. The system was examined at from temperatures 15·25°, 40°, 50° and 70° and the results are given in Tables D, E, F, G below.

NOTE.—For the examination of the system at 15·25°, water at this constant temperature was made to flow through the vessel D.

The results are expressed as before and they are plotted in Graph II.

### Table D.—Temperature 15·25°.

| No. | Concentration of benzene. | Pressure. | No. | Concentration of benzene. | Pressure. |
|---|---|---|---|---|---|
| 1 | 0·1216 | 0·226 | 9 | 0·1770 | 5·965 |
| 2 | 0·1355 | 0·317 | 10 | 0·1825 | 5·965 |
| 3 | 0·1485 | 0·541 | 11 | 0·1729 | 4·900 |
| 4 | 0·1590 | 0·904 | 12 | 0·1676 | 1·976 |
| 5 | 0·1653 | 1·448 | 13 | 0·1634 | 1·082 |
| 6 | 0·1695 | 2·967 | 14 | 0·1472 | 0·493 |
| 7 | 0·1740 | 5·755 | 15 | 0·1240 | 0·230 |
| 8 | 0·1743 | 5·908 | 16 | 0·0284 | 0·000 |

Nos. 1–10—" Ascending " points. Nos. 11–16—" Descending " points.

### Table E.—Temperature 40°.

| No. | Concentration of benzene. | Pressure. | No. | Concentration of benzene. | Pressure. |
|---|---|---|---|---|---|
| 1 | 0·1205 | 0·764 | 9 | 0·1732 | 18·277 |
| 2 | 0·1289 | 1·086 | 10 | 0·1696 | 17·484 |
| 3 | 0·1486 | 2·416 | 11 | 0·1682 | 14·417 |
| 4 | 0·1604 | 5·178 | 12 | 0·1659 | 10·745 |
| 5 | 0·1620 | 6·688 | 13 | 0·1637 | 8·163 |
| 6 | 0·1636 | 8·439 | 14 | 0·1620 | 6·349 |
| 7 | 0·1651 | 10·045 | 15 | 0·1586 | 4·492 |
| 8 | 0·1683 | 14·803 | 16 | 0·1345 | 1·313 |

Nos. 1–9—" Ascending " points. Nos. 10–16—" Descending " points.

### Table F.—Temperature 50°.

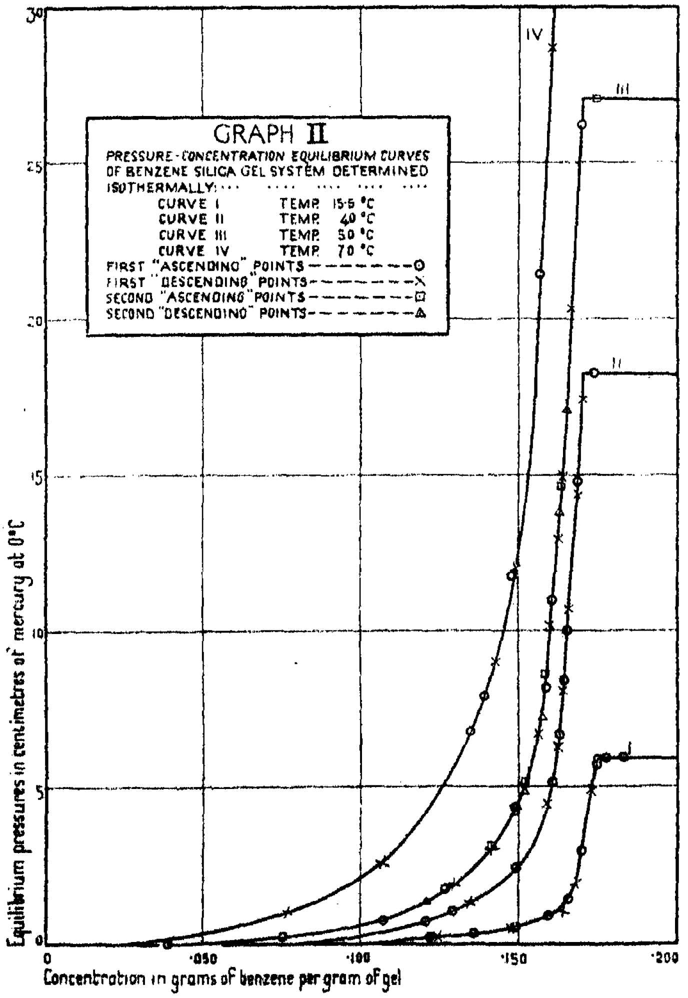
| No. | Concentration of benzene. | Pressure. | No. | Concentration of benzene. | Pressure. |
|---|---|---|---|---|---|
| 1 | 0·0383 | 0·044 | 14 | 0·1486 | 4·290 |
| 2 | 0·0750 | 0·249 | 15 | 0·1410 | 3·029 |
| 3 | 0·1071 | 0·879 | 16 | 0·1291 | 1·911 |
| 4 | 0·1268 | 1·774 | 17 | 0·1413 | 3·107 |
| 5 | 0·1487 | 4·376 | 18 | 0·1519 | 5·202 |
| 6 | 0·1580 | 8·205 | 19 | 0·1586 | 8·647 |
| 7 | 0·1606 | 10·972 | 20 | 0·1633 | 14·627 |
| 8 | 0·1718 | 26·3 | 21 | 0·1741 | 27·088 |
| 9 | 0·1662 | 20·346 | 22 | 0·1646 | 17·117 |
| 10 | 0·1637 | 14·927 | 23 | 0·1630 | 13·841 |
| 11 | 0·1622 | 12·990 | 24 | 0·1566 | 7·267 |
| 12 | 0·1596 | 10·256 | 25 | 0·1515 | 4·913 |
| 13 | 0·1560 | 6·746 | 26 | 0·1205 | 1·402 |

Nos. 1–8—First " ascending " points. Nos. 9–16—First " descending " points.
Nos. 17–21—Second " ascending " points. Nos. 22–26—Second " descending " points.

Table G.—Temperature 70°.

| No. | Concentration of benzene. | Pressure. | No. | Concentration of benzene. | Pressure. |
|---|---|---|---|---|---|
| 1 | 0·1345 | 6·809 | 8 | 0·1718 | 54·659 |
| 2 | 0·1390 | 7·939 | 9 | 0·1603 | 28·705 |
| 3 | 0·1479 | 11·772 | 10 | 0·1490 | 11·998 |
| 4 | 0·1565 | 21·461 | 11 | 0·1429 | 9·046 |
| 5 | 0·1604 | 30·247 | 12 | 0·1067 | 2·600 |
| 6 | 0·1671 | 52·327 | 13 | 0·0765 | 1·046 |
| 7 | 0·1904 | 54·659 | | | |

Nos. 1–7—"Ascending" points. Nos. 8–13—"Descending" points.



The isothermals representing the pressure-concentration equilibria between benzene and silica gel are strikingly different from those obtained for the closely analogous system benzene and ferric oxide gel.

At the four temperatures examined the pressure-concentration isothermals are definitely repeatable and reversible over the whole range of concentration from zero up to saturation. The purity of the gaseous phase and the reliability of our experimental methods are shown by a comparison of the vapour pressures obtained at saturation with the vapour pressures determined for pure benzene by Young and by Regnault.

| Temperature. | Equilibrium pressures obtained at saturation. | Vapour pressure of pure benzene. | |
|---|---|---|---|
| | | Young. | Regnault. |
| °<br>40 | cms.<br>18·277 | 18·108 | 18·362 |
| 50 | 27·088 | 26·897 | 27·137 |
| 70 | 54·659 | 54·740 | 54·742 |

Careful experiments were made over the whole range of pressures and concentrations in order to see if temporary cooling of the system to room temperature, or temporary heating to 78°, produced any effect on the equilibrium pressure after restoration of the system to its original controlled constant temperature. In no case was any appreciable difference found between the equilibrium pressures obtained before or after such disturbances.

Further, interruption of the smooth addition of benzene by occasional withdrawals or interruption of the smooth withdrawal by occasional additions produced no departure from the equilibria represented by the isothermals.

There would seem to be no doubt, therefore, that these isothermals represent real pressure-concentration equilibria throughout the whole range of pressures and concentrations and that the equilibria are completely reversible.

The adsorptive processes for benzene of the two analogous dehydrated gels—ferric oxide gel and silica gel—are thus proved to be essentially different.

Experiments are now in progress on the relationships between these same gels and (1) water, (2) permanent and semi-permanent gases and gas mixtures. The work will be published in later Parts of this research on gas-solid equilibria and it is thought better to postpone the theoretical consideration of the results of Parts I and II until a later stage of the work.

# *The Triplets of Helium.*

By J. A. Gaunt, Trinity College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received November 6, 1928.)

## 1. *Introduction.*

A theory of the helium atom was developed by Heisenberg,* following his famous principle of "resonance." His work is based upon Schrödinger's equation, and in order to allow for the spin of the electrons he introduces extra energy terms, expressing the classical energy of two appropriate magnets. It is the perturbation by this spin energy which produces the triplet separations. Heisenberg's calculation of these separations is open to three criticisms: (1) He assumes that certain simple forms are correct first approximations to the wave-functions; whereas, owing to degeneracy, it is necessary to take linear combinations of these forms. (2) He estimates the mean values of the spin energy by means of a model built up of precessing vectors. (3) He neglects the radius of the inner orbit in comparison with that of the outer orbit, even when the principal quantum number of the latter is only 2; this is the least satisfactory of several necessary simplifications.

Schrödinger's equation is likely to be supplanted as the foundation of wave-mechanics by the equation recently put forward by Dirac.† This fits the spin of the electron neatly into the theory of relativity, and produces the doublets of the hydrogen-like atom in a beautiful manner. Dirac's $q$-number theory has been translated into wave-mechanics by Darwin.‡ Apart altogether from the above criticisms of Heisenberg, it seemed expedient to proceed to the theory of an atom with two electrons on the basis of the new equation. Calculations which are independent of the spin, such as the approximate energy-levels, and the separation between ortho- and para-terms, are the same on either theory, and are not the concern of this paper. We deal here with spin effects, such as the fine structure of the triplets and intercombinations between ortho- and para-states.

It was suggested that the new theory might modify the classification or selection rules in such a way as to explain the spectra of the gaseous nebulæ. There are lines in these spectra which probably arise from transitions between ortho- and para-states of $O^{++}$ and $N^{+}$—systems with two series electrons. For this reason, special attention is paid to ortho-para transitions, and a section is devoted to the triplet of $O^{++}$ concerned. The result is no new permission of the " forbidden " lines. This does not mean that they are rigorously excluded by the theory, but that the probability of such transitions is very small and requires for its evaluation approximations of a higher order than those of this paper. If under special conditions all other means of escape from the " metastable " state (*e.g.*, collisions) were even more improbable, then the emission of " forbidden " lines would become important.

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* Heisenberg, 'Z. f. P.,' vol. 39, p. 499 (1926).

† Dirac, 'Roy. Soc. Proc.,' A, vol. 117, p. 610 (1928); also *ibid.*, vol. 118, p. 351 (1928).

‡ Darwin 'Roy. Soc. Proc.,' A, vol. 118, p. 654 (1928).

There are two main differences between our methods and Heisenberg's. Whereas he first applies the perturbation by the electrostatic interaction of the electrons with a complete neglect of spin, and then superposes the much smaller spin perturbation, in our case part of the spin effect is included from the start in Dirac's equation. This calls for a perturbation theory for nearly degenerate systems, which is the subject of §§ 3 and 4. It is much the same as the ordinary perturbation theory.

Secondly, the spin energies are calculated in a straightforward manner by means of integrals involving the wave-functions, and are not taken from a mechanical model. The details of these calculations will be published elsewhere. The method for a helium atom with one excited electron is sketched in § 6, and the resulting triplet separations are given in § 7. § 8 is a brief note on the classification and selection rules, and § 9 summarises the parallel work on the deepest triplet of $O^{++}$.

The spin energy terms used in the perturbation theory are practically the same as Heisenberg's, with the omission of those which are already accounted for in Dirac's equation. It is shown, however, in § 5 that this energy not only corresponds with classical theory, but also arises naturally from the theory of Dirac. It is there suggested that the exact interaction energy of two electrons has the simple form $\frac{e^2}{r}[1 - \rho_1'\rho_2'(\sigma_1\sigma_2)]$ (the notation is explained below), and that the more complicated form used is an approximation better suited to the calculations in hand.

## 2. *Notation and General Method.*

We shall use, with a few modifications, the notation of Dirac and Darwin. Our method is more closely related to that of Darwin's paper than to that of Dirac's, being wave-mechanics and not $q$-number theory. The quantum number $j$ has two meanings; where it is used in Dirac's sense we shall say so;

otherwise its meaning is that of the ordinary classification of spectra. It saves some periphrasis in discussions on orders of magnitude to use a unit of energy comparable with the ionisation energy of the atom. We use $h$, not $2\pi h$, for Planck's constant.

Each of the two electrons in the atom has four co-ordinates: $x\ y\ z$ denoting position in space, and a fourth co-ordinate connected with the spin. The last has four characteristic values, so that for a single electron each wave-function consists of four functions of position. It is unnecessary to inquire into the nature of the spin co-ordinate, or its characteristic values, so long as these are given a definite order which is maintained throughout the theory.

The co-ordinates of the two electrons are distinguished by suffixes 1, 2. For this reason, Dirac's spin matrices $\sigma_1$, $\sigma_2$, $\sigma_3$, $\rho_1$, $\rho_2$, $\rho_3$, are replaced by $\sigma_x$, $\sigma_y$, $\sigma_z$, $\rho'$, $\rho''$, $\rho'''$. This notation is chosen because the three $\sigma$'s behave like the components of a vector $\boldsymbol{\sigma}$. The spin-co-ordinate is chosen so that the matrices in its scheme of the $\sigma$'s and $\rho$'s are those given by Dirac (p. 614), and used by Darwin.

$$\left.\begin{array}{lll}
\sigma_x = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \sigma_y = \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix} & \sigma_z = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \\
\rho' = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} & \rho'' = \begin{pmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{pmatrix} & \rho''' = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}
\end{array}\right\} . \quad (2.0)$$

The natural way to solve the two-electron problem is as follows. A wave-function and energy are found for each electron separately in a central field V, which represents as nearly as possible the field of the other electron as well as that of the nucleus. It preserves the symmetry and simplifies the theory if the same central field is used for each wave-function; though it may be more accurate in practice to use two different equations, as in Hartree's method.* The separate wave-functions are then combined into anti-symmetrical functions, and perturbed by the various terms of the interaction energy less the difference between the central field used and that of the nucleus. This perturbation may be carried to any desired order.

If the two separate wave-functions $\psi_a$, $\psi_b$, in the central field of potential

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* Hartree, 'Proc. Camb. Phil. Soc.,' vol. 24, p. 89 (1928).

V, have time-factors $\exp - (mc^2 + E_a)\, it/h$ and $\exp - (mc^2 + E_b)\, it/h$, then they satisfy Dirac's equations

$$\left.\begin{aligned}\left[mc + \frac{E_a + eV}{c} + \rho'(\sigma \cdot p) + \rho'''mc\right]\psi_a = 0 \\ \left[mc + \frac{E_b + eV}{c} + \rho'(\sigma \cdot p) + \rho'''mc\right]\psi_b = 0\end{aligned}\right\}. \qquad (2.1)$$

In the absence of any interaction, the total wave-function would be

$$\Psi = \psi_a(1)\,\psi_b(2) - \psi_a(2)\,\psi_b(1) \qquad (2.2)$$

where "1," "2" summarise the co-ordinates of the respective electrons. Its time-factor is $\exp - (2mc^2 + E)\, it/h$ where

$$E = E_a + E_b, \qquad (2.3)$$

and it satisfies the equation

$$\left[2mc + \frac{E + eV(1) + eV(2)}{c} + \rho_1'(\sigma_1 \cdot p_1) + \rho_2'(\sigma_2 \cdot p_2) + \rho_1'''mc + \rho_2'''mc\right]\Psi = 0. \qquad (2.4)$$

Our assumption is that the correct equation for an atom with two electrons is to be obtained from (2.4) by subtracting two perturbing energy terms P and S from the numerator of the second term. P depends upon the space-co-ordinates alone, and apart from a negligible term.

$$P - eV(1) - eV(2) = \frac{e^2}{r} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}, \qquad (2.5)$$

where $r$ is the distance between the electrons and $Ze$ is the charge on the nucleus. S is discussed in § 5. It involves the spins.

We are concerned in this paper with the perturbation by S and not the perturbation by P. We assume that V has been chosen in the most favourable manner possible, or, alternatively, that Hartree's method has been used, with the equations:

$$\left.\begin{aligned}\left[mc + \frac{E_a + eV_a}{c} + \rho'(\sigma \cdot p) + \rho'''mc\right]\psi_a = 0 \\ \left[mc + \frac{E_b + eV_b}{c} + \rho'(\sigma \cdot p) + \rho'''mc\right]\psi_b = 0\end{aligned}\right\}, \qquad (2.6)$$

$$V_a(1) = -\int \frac{e\,|\psi_b(2)|^2}{r} + \frac{Ze}{r_1}, \quad V_b(1) = -\int \frac{e\,|\psi_a(2)|^2}{r} + \frac{Ze}{r_1}$$

(normalised $\psi$'s). (2.7)

The perturbations relevant to this method have been discussed by the author.* There is a large first order correction to the energy, $\Delta E$, due to double counting of the mutual potential energy of the electrons; but the matrix components of $P - \Delta E$ are reduced to a minimum. They cannot, of course, be reduced below the order of the separation between para- and ortho-terms, which they produce. In the succeeding sections, " of the order of P " is to be understood as meaning " of the order of the matrix-components of $P - \Delta E$, or of the ortho-para separation."

While P is of the order of 1/10, S is much smaller, of the order of the separations within the triplets. It is suitably measured by $\gamma^2$, where $\gamma$ is the fine structure constant $2\pi e^2/ch = 7\cdot 10^{-3}$. It does not include, as did Heisenberg's spin energy, the two terms due to the motion of the electron-magnets in the central field. This energy is already allowed for in (2.1). The result is a formal difference in the theory. Where Heisenberg in his first approximation had two $\psi_a$'s with the same energy but different spins, combining with two $\psi_b$'s to form a triplet and a singlet, we have from (2.1) two $\psi_a$'s (or $\psi_b$'s) with nearly equal but slightly different energies. The difference, being of the order of S, is small compared with P. Our first step, therefore, is to construct a theory of the perturbation of nearly degenerate systems.

## 3. *Perturbation Theory.*

Abbreviate (2.4) to

$$[F + E/c]\,\Psi = 0. \tag{3.00}$$

Suppose that it has a number of antisymmetrical solutions $\Psi_m$ whose energies are nearly equal to E.

$$E_m = E + \delta E_m, \qquad \delta E_m = O(S). \tag{3.01}$$

The other solutions $\Psi_n$ have quite different energies.

It is often convenient to use unnormalised wave-functions. Let

$$\int |\Psi_m|^2 = C_m, \text{ etc.} \tag{3.02}$$

where $\int$ denotes an integration over all space and a summation for the four values of each spin co-ordinate.

The perturbed equation is

$$\left[F + \frac{E - P - S}{c}\right]\Psi = 0. \tag{3.10}$$

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* Gaunt, 'Proc. Camb. Phil. Soc.,' vol. 24, p. 382 (1928).

It will have solutions with energies nearly equal to E

$$E^\mu = E + \Delta E^\mu + \delta E^\mu. \tag{3.11}$$

Their difference from E has been divided into two parts, of which $\Delta E^\mu$ may be considered to be due to P, and $\delta E^\mu$ to S and the $\delta E_m$'s. The wave-function has an expansion in terms of the unperturbed wave-functions, which is conveniently written as

$$\Psi_\mu = \sum_m (a_m{}^\mu + \delta a_m{}^\mu)\, \Psi_m + \sum_n (a_n{}^\mu + \delta a_n{}^\mu)\, \Psi_n. \tag{3.12}$$

By substitution in (3.10) and use of (3.00) we get

$$\sum_m (\Delta E^\mu + \delta E^\mu - \delta E_m - P - S)\,(a_m{}^\mu + \delta a_m{}^\mu)\, \Psi_m \\ + \sum_n (E^\mu - E_n - P - S)\,(a_n{}^\mu + \delta a_n{}^\mu)\, \Psi_n = 0. \tag{3.20}$$

We can now choose the $a$'s to be the coefficients in the absence of spin-effects, so that (3.20) is satisfied when $\delta E^\mu$, $\delta E_m$, S, $\delta a_m{}^\mu$, $\delta a_n{}^\mu$ all vanish. This corresponds to carrying out the perturbation by P to all orders in the old theory. Nothing is gained, but no harm is done, by going beyond that order whose effect is just greater than that of the spin perturbation. Subtracting from (3.20) the terms independent of spin,

$$\sum_m \{(\delta E^\mu - \delta E_m - S)\,(a_m{}^\mu + \delta a_m{}^\mu) + (\Delta E^\mu - P)\,\delta a_m{}^\mu\}\, \Psi_m \\ + \sum_n \{(\delta E^\mu - S)\,(a_n{}^\mu + \delta a_n{}^\mu) + (E + \Delta E^\mu - E_n - P)\,\delta a_n{}^\mu\}\, \Psi_n = 0. \tag{3.21}$$

The $a_m{}^\mu$'s are of order unity, and the $a_n{}^\mu$'s of the order of P, as is shown by (3.20). Thus (3.21) shows that the $\delta a_m{}^\mu$'s are of the order of S/P and the $\delta a_n{}^\mu$'s of the order of S. We require only a first approximation to the effect of the spin, so we reduce (3.21) to

$$\sum_m \{(\delta E^\mu - \delta E_m - S)\, a_m{}^\mu + (\Delta E^\mu - P)\,\delta a_m{}^\mu\}\, \Psi_m \\ + \sum_n (E - E_n)\,\delta a_n{}^\mu\, \Psi_n = 0. \tag{3.22}$$

Multiply by $\overline{\Psi}_{m'}$ and integrate.

$$(\delta E^\mu - \delta E_{m'})\, C_{m'}\, a_{m'}{}^\mu - \sum_m S_{mm'}\, a_m{}^\mu + \Delta E^\mu C_{m'}\, \delta a_{m'}{}^\mu - \sum_m P_{mm'}\, \delta a_m{}^\mu = 0 \tag{3.23}$$

where

$$S_{mm'} \equiv \int (S\, \Psi_m)\, \overline{\Psi}_{m'}, \text{ etc.} \tag{3.24}$$

There is a corresponding equation determining the $\delta a_n{}^\mu$'s, but they are unimportant.

Since we require only a first approximation to $\delta a_m^\mu$ (neglecting S in comparison with S/P), it is sufficient to use a first approximation to $a_m^\mu$ in (3.23). Taking (3.20) to this order only,

$$\sum_m (\Delta E^\mu - P)\, a_m^\mu\, \Psi_m + \sum_n (E - E_n)\, a_n^\mu\, \Psi_n = 0,$$

so that

$$\Delta E^\mu C_{m'}\, a_{m'}^\mu - \Sigma\, P_{mm'}\, a_m^\mu = 0. \tag{3.25}$$

One further approximation does not alter the order of accuracy. The solutions of (2.1) have four components, of which the first two are of the order of $\gamma$ in comparison with the last two, while these differ from solutions of Schrödinger's equation by a fraction of the order of $\gamma^2$. Consequently we may put

$$\Psi_m = \psi_m + \delta\psi_m, \tag{3.26}$$

where for 12 components $\psi_m = 0$ and $\delta\psi_m = O(\gamma)$; and for the other 4, $\psi_m$ satisfies the Schrödinger equation corresponding to (2.4) and is taken to be of the order unity, and $\delta\psi_m = O(\gamma^2)$. In calculating $P_{mm'}$, small components of $\Psi_m$ are multiplied by small components of $\Psi_{m'}$, since P does not involve the spins ; also in § 5 S will be so arranged that the same is true of the calculation of $S_{mm'}$. Hence we are only neglecting $\gamma^2$ in comparison with unity if we use in (3.23), (3.25) :

$$C_m = \int |\psi_m|^2, \quad S_{mm'} = \int \bar{\psi}_{m'}\, S\psi_m, \quad P_{mm'} = \int \bar{\psi}_{m'}\, P\psi_m. \tag{3.27}$$

The result is that (3.25) is the ordinary equation in the first order perturbation of Heisenberg's theory. We shall therefore take the $\Delta E^\mu$'s and other consequences of this equation as known, and use this knowledge to eliminate $P_{mm'}$ and $\delta a_m^\mu$ from (3.23).

## 4. *The Spin Perturbation and Intercombinations.*

The normal term will be denoted by a suffix 0. It is not degenerate ; that is, there is only one "*m*." The only part which is not symmetrical in the position co-ordinates of the two electrons must contain $\delta a_n$'s, which are negligible (of the order of S instead of S/P). Thus the main part of the combinations between ortho-terms and the normal term must be contributed by the perturbations of the former.

Most other terms appear in groups of four. Owing to accidental degeneracies the number of *m*'s in any case may be manifold ; but for each $\mu$ there are only four non-vanishing $a_m^\mu$'s. We pick out four $\mu$'s which involve the same four

$m$'s and label then I, II, III, IV. Of these the first three have wave-functions antisymmetrical in the position co-ordinates and symmetrical in the spins, while the fourth wave-function is symmetrical in the positions and antisymmetrical in the spins. Also, $\Delta E^{I} = \Delta E^{II} = \Delta E^{III} \neq \Delta E^{IV}$, so that there is still a double degeneracy. This means that when $\Delta E^{\mu} = \Delta E^{I}$ the four equations (3.25) corresponding to the four values of $m'$ are all equivalent; and this one equation is the only one connecting the four $a_m{}^{\mu}$'s ($\mu =$ I, II, or III), which are triply indeterminate until the spin perturbations are used. Another form of this equation is obtained by expressing the fact that these three terms do not combine with the normal state to a first approximation.

Let X be any symmetrical function of the positions of the two electrons. It may be taken to be the electric moment of the atom, since that is what we shall want for radiation. Then by considerations of symmetry

$$X_{I0} = 0 \quad \text{(first approximation).} \tag{4.00}$$

That is:

$$\sum_m a_m{}^{I} X_{m0} = 0, \tag{4.01}$$

and this equation must be equivalent to

$$\Delta E^{I} C_{m'} a_{m'}{}^{I} - \sum_m P_{mm'} a_m{}^{I} = 0,$$

so that

$$\begin{aligned} X_{m0} : -P_{mm'} &= X_{m'0} : \Delta E^{I} \,.\, C_{m'} - P_{m'm'} \quad (m \neq m') \\ &= x_{m'} \text{ (say)} \end{aligned} \tag{4.02}$$

Including the spin terms, we have the second approximation

$$X_{I0} = \sum_m \delta a_m{}^{I} X_{m0} \tag{4.10}$$

$$= x_{m'} \left\{ \Delta E^{I} C_{m'} \, \delta a_{m'}{}^{I} - \sum_m P_{mm'} \, \delta a_m{}^{I} \right\} \quad \text{(by (4.02))}$$

$$= -x_{m'} \left\{ (\delta E^{I} - \delta E_{m'}) C_{m'} a_{m'}{}^{I} - \sum_m S_{mm'} a_m{}^{I} \right\} \tag{4.11}$$

by (3.23).

The fourth term does combine with the normal term to a first approximation; and

$$X_{IV0} = \sum_m a_m{}^{IV} X_{m0}$$

$$= x_{m'} \left\{ \Delta E^{I} C_{m'} a_{m'}{}^{IV} - \sum_m P_{mm'} a_m{}^{IV} \right\} \quad \text{(by (4.02))}$$

$$= x_{m'} (\Delta E^{I} - \Delta E^{IV}) C_{m'} a_{m'}{}^{IV} \tag{4.12}$$

by (3.25). Eliminating $x_{m'}$ from (4.11), (4.12):

$$(\delta E^{I} - \delta E_{m'}) C_{m'} a_{m'} - \sum_m S_{mm'} a_m{}^{I} = \frac{X_{I0}}{X_{IV0}} (\Delta E^{IV} - \Delta E^{I}) C_{m'} a_{m'}{}^{IV}. \tag{4.13}$$

The coefficients $a_m{}^{\mathrm{IV}}$ are known. Since the wave-functions are not normalised, the ratio $X_{\mathrm{I}0} : X_{\mathrm{IV}0}$ is arbitrary. Were $\delta E^{\mathrm{I}}$ known, the equations (4.13) would determine $a_m{}^{\mathrm{I}}$ in terms of this ratio, and so the normalising factor $C_{\mathrm{I}}$. We then have the ratio $X_{\mathrm{I}0}{}^2/C_{\mathrm{I}} : X_{\mathrm{IV}0}{}^2/C_{\mathrm{IV}}$ ($C_{\mathrm{IV}}$ being known), which is what we require for comparing intensities of lines.

Let $\Delta$ be the determinant of the coefficients on the left-hand side of (4.13). It has diagonal terms $\delta E^{\mathrm{I}} - \delta E_m - S_{mm}$, and non-diagonal terms $-S_{mm'}$. Let $\Delta_{mm'}$ be the cofactor of the corresponding term. Then (4.13) gives

$$\Delta \,.\, a_m{}^{\mathrm{I}} = \frac{X_{\mathrm{I}0}}{X_{\mathrm{IV}0}} (\Delta E^{\mathrm{IV}} - \Delta E^{\mathrm{I}}) \sum_{m'} C_{m'} a_{m'}{}^{\mathrm{IV}} \Delta_{mm'}. \qquad (4.20)$$

We can now use the fact that $\psi_{\mathrm{I}}$ and $\psi_{\mathrm{IV}}$ are orthogonal, so that

$$\sum_m C_m a_m{}^{\mathrm{IV}} a_m{}^{\mathrm{I}} = 0. \qquad (4.21)$$

Substituting from (4.20), either $X_{\mathrm{I}0} = 0$, or

$$\sum_{m,\, m'} C_m a_m{}^{\mathrm{IV}} C_{m'} a_{m'}{}^{\mathrm{IV}} \Delta_{mm'} = 0. \qquad (4.22)$$

If $X_{\mathrm{I}0} = 0$, we have five homogeneous equations (4.13) and (4.21), and all the determinants

$$\sum_m C_m a_m{}^{\mathrm{IV}} \Delta_{mm'}$$

must vanish, to give non-vanishing $a_m{}^{\mathrm{I}}$'s; so (4.22) is still true. It is a cubic in $\delta E^{\mathrm{I}}$, and may be written as a bordered determinant

$$\begin{vmatrix} 0 & C_m a_m{}^{\mathrm{IV}} \\ C_m a_m{}^{\mathrm{IV}} & \Delta \end{vmatrix} = 0. \qquad (4.23)$$

The same equation holds for II and III, and its three roots are $\delta E^{\mathrm{I}}$, $\delta E^{\mathrm{II}}$, $\delta E^{\mathrm{III}}$.

Our procedure, then, is to calculate the terms of $\Delta$ and solve (4.23). This gives the fine structure of the triplet. (4.20) then determines the wave-functions and their normalising factors, unless $\Delta = 0$. If $\Delta = 0$ and $X_{\mathrm{I}0} \neq 0$, (4.20) shows that the determinants

$$\sum_{m'} C_{m'} a_{m'}{}^{\mathrm{IV}} \Delta_{mm'}$$

must vanish, so that the matrix of equations (4.13), (4.21) must be of the third (or lower) rank. This implies a number of equations such as

$$\begin{vmatrix} 0 & C_{m'} a_{m'}{}^{\mathrm{IV}} \\ C_{m'} a_{m'}{}^{\mathrm{IV}} & \Delta_{mn} \end{vmatrix} = 0 \quad (m' \text{ takes all values but } m). \qquad (4.30)$$

In general, these determinants do not all vanish, so that

$$\text{if } \Delta = 0, \quad X_{\text{I}0} = 0, \tag{4.31}$$

and there is no intercombination of the order of our approximations.

We have assumed above that $X_{\text{IV}0} \neq 0$. It will always be possible to find some symmetrical function X for which this is true. Equations (4.11) (4.12) show that if $X_{\text{IV}0}$ vanishes to a first approximation, $X_{\text{I}0}$ vanishes to a second approximation.

## 5. *The Spin Energy.*

Heisenberg writes down the following spin energy terms for electrons with magnetic moments $\frac{e}{mc}\,\mathbf{s}_1$, $\frac{e}{mc}\,\mathbf{s}_2$ and a nucleus of charge $Ze$.

$$\begin{aligned}
&-\frac{Ze^2}{mc^2}\frac{[\mathbf{r}_1\mathbf{v}_1]}{r_1^{\,3}}\cdot\mathbf{s}_1 + \frac{e^2}{mc^2}\frac{[\mathbf{r}_1-\mathbf{r}_2,\,\mathbf{v}_1-\mathbf{v}_2]}{r^3}\cdot\mathbf{s}_1\\
&-\frac{Ze^2}{mc^2}\frac{[\mathbf{r}_2\mathbf{v}_2]}{r_2^{\,3}}\cdot\mathbf{s}_2 + \frac{e^2}{mc^2}\frac{[\mathbf{r}_2-\mathbf{r}_1,\,\mathbf{v}_2-\mathbf{v}_1]}{r^3}\cdot\mathbf{s}_2\\
&+\frac{Ze^2}{2mc^2}\frac{[\mathbf{r}_1\mathbf{v}_1]}{r_1^{\,3}}\cdot\mathbf{s}_1 - \frac{e^2}{2mc^2}\frac{[\mathbf{r}_1-\mathbf{r}_2,\,\mathbf{v}_1]}{r^3}\cdot\mathbf{s}_1\\
&+\frac{Ze^2}{2mc^2}\frac{[\mathbf{r}_2\mathbf{v}_2]}{r_2^{\,3}}\cdot\mathbf{s}_2 - \frac{e^2}{2mc^2}\frac{[\mathbf{r}_2-\mathbf{r}_1,\,\mathbf{v}_2]}{r^3}\cdot\mathbf{s}_2\\
&\qquad\qquad+\left(\frac{e}{mc}\right)^2\frac{(\mathbf{s}_1\mathbf{s}_2)-3\,(\mathbf{s}_1\mathbf{r}_0)\,(\mathbf{s}_2\mathbf{r}_0)}{r^3},
\end{aligned}\tag{5.00}$$

where $\mathbf{r}_0 = \frac{\mathbf{r}_1-\mathbf{r}_2}{r}$, and $r$ is the distance between the electrons. The first line expresses the energy of the magnetic moment of the first electron due to its motion through the field of the nucleus and to its motion relative to the second electron in the electrostatic field of this electron. The third line is Thomas' correction to the energy of the first line, which is relative to moving axes. The second and fourth lines deal similarly with the magnetic moment of the second electron, and the last line expresses the interaction of the two magnets. We shall group the terms differently.

$$\begin{aligned}
&-\frac{Ze^2}{2mc^2}\frac{[\mathbf{r}_1\mathbf{v}_1]}{r_1^{\,3}}\cdot\mathbf{s}_1 + \frac{e^2}{2mc^2}\frac{[\mathbf{r}_1-\mathbf{r}_2,\,\mathbf{v}_1]}{r^3}\cdot\mathbf{s}_1\\
&-\frac{Ze^2}{2mc^2}\frac{[\mathbf{r}_2\mathbf{v}_2]}{r_2^{\,3}}\cdot\mathbf{s}_2 + \frac{e^2}{2mc^2}\frac{[\mathbf{r}_2-\mathbf{r}_1,\,\mathbf{v}_2]}{r^3}\cdot\mathbf{s}_2\\
&+\frac{e^2}{mc^2}\frac{[\mathbf{r}_2-\mathbf{r}_1,\,\mathbf{v}_2]}{r^3}\cdot\mathbf{s}_1 + \frac{e^2}{mc^2}\frac{[\mathbf{r}_1-\mathbf{r}_2,\,\mathbf{v}_1]}{r^3}\cdot\mathbf{s}_2\\
&\qquad\qquad+\left(\frac{e}{mc}\right)^2\frac{(\mathbf{s}_1\mathbf{s}_2)-3\,(\mathbf{s}_1\mathbf{r}_0)\,(\mathbf{s}_2\mathbf{r}_0)}{r^3}.
\end{aligned}\tag{5.01}$$

In this expression the first line is the energy (with Thomas' correction) of the first electron-magnet in the combined electrostatic fields of the nucleus and the other electron. In so far as the non-Coulomb field of (2.1) is an adequate substitute for these combined fields, this part of Heisenberg's spin-energy is already implicit in that equation. The error due to using the spin-energy given by Dirac's theory of a single electron should be as small as SP. So for the second line of (5.01), which applies to the second electron-magnet.

The last two lines give S. In Dirac's theory, the electron behaves as if it had a magnetic moment $-\frac{eh}{4\pi mc}\boldsymbol{\sigma}$. We substitute this for $\frac{e}{mc}\mathbf{s}$, and $\frac{1}{m}\mathbf{p}$ for $\mathbf{v}$.

$$S = -\frac{e^2h}{4\pi m^2c^2}\left\{\left[\frac{\mathbf{r}_2-\mathbf{r}_1}{r^3},\ \mathbf{p}_2\right].\boldsymbol{\sigma}_1+\left[\frac{\mathbf{r}_1-\mathbf{r}_2}{r^3},\ \mathbf{p}_1\right].\boldsymbol{\sigma}_2\right\}$$
$$+\left(\frac{eh}{4\pi mc}\right)^2\frac{(\boldsymbol{\sigma}_1.\boldsymbol{\sigma}_2)-3(\boldsymbol{\sigma}_1.\mathbf{r}_0)(\boldsymbol{\sigma}_2.\mathbf{r}_0)}{r^3} \qquad (5.02)$$

$$= T_1+T_2+U \qquad \text{(say).} \qquad (5.03)$$

There are some non-commuting $q$-numbers in $T_1$ and $T_2$, but these terms are real, for

$$\left[\frac{\mathbf{r}_2-\mathbf{r}_1}{r^3},\ \mathbf{p}_2\right]+\left[\mathbf{p}_2,\ \frac{\mathbf{r}_2-\mathbf{r}_1}{r^3}\right]=-\frac{ih}{2\pi}\left[\nabla_2,\ -\nabla_2\frac{1}{r}\right]=0, \qquad (5.04)$$

*i.e.*, the imaginary part of the vector product vanishes; also it commutes with $\boldsymbol{\sigma}_1$.

We can approach the question of the spin energy terms along quite a different route. S can be interpreted as arising from the action on the electrons of each other's magnetic field. For instance, $T_1$ is the energy of the first electron-magnet in the magnetic field due to the motion of the second electron's charge.

Now when a single electron moves in a magnetic field whose vector potential is $\mathbf{A}$, $\mathbf{p}$ must be replaced by $\mathbf{p}+\frac{e}{c}\mathbf{A}$ in Dirac's equation (2.1). The additional energy W $(=cp_0)$ required to balance this extra term is

$$-e\rho'(\boldsymbol{\sigma}.\mathbf{A}), \qquad (5.10)$$

$\mathbf{A}$ will depend on the position only of the given electron.

(5.10) is inconvenient for our purpose, since $\rho'$ mixes the first two components of the wave-function with the last two, so that we cannot neglect the former without reducing the whole perturbation to zero. In this section let us denote the four components of a wave-function by suffixes 1, 2, 3, 4. In finding the matrix-components of the spin perturbation we are concerned with integrals of sums such as

$$-\Sigma\, \bar{\psi}_b e\rho' (\sigma \,.\, \mathrm{A})\, \psi_a, \tag{5.11}$$

where (5.10) operates on $\psi_a$, and the summation is over corresponding components of $\psi_a$, $\bar{\psi}_b$.

On carrying out the operation with $\rho'$, (5.11) becomes

$$-\{\bar{\psi}_{b1} e (\sigma \,.\, \mathrm{A})\, \psi_{a3} + \bar{\psi}_{b2} e (\sigma \,.\, \mathrm{A})\, \psi_{a4} + \bar{\psi}_{b3} e (\sigma \,.\, \mathrm{A})\, \psi_{a1} + \psi_{b4} e (\sigma \,.\, \mathrm{A})\, \psi_{a2}\}. \tag{5.12}$$

The operation with $\sigma$ replaces each of the large wave-functions $\psi_3$, $\psi_4$, by a large wave-function, and each of the small functions $\psi_1$, $\psi_2$ by a small one. It is sufficient therefore to substitute for the small functions explicit in (5.12) in order to get rid of them altogether.

Carrying out the operations with $\rho'$, $\rho'''$ in the first two components of (2.1)

$$\left.\begin{aligned} \left(2mc + \frac{\mathrm{E}_a + e\mathrm{V}}{c}\right) \psi_{a1} + (\sigma \,.\, \mathbf{p})\, \psi_{a3} = 0 \\ \left(2mc + \frac{\mathrm{E}_a + e\mathrm{V}}{c}\right) \psi_{a2} + (\sigma \,.\, \mathbf{p})\, \psi_{a4} = 0 \end{aligned}\right\}, \tag{5.13}$$

or with sufficient accuracy

$$\left.\begin{aligned} \psi_{a1} = -\frac{1}{2mc} (\sigma \,.\, \mathbf{p})\, \psi_{a3} \\ \psi_{a2} = -\frac{1}{2mc} (\sigma \,.\, \mathbf{p})\, \psi_{a4} \end{aligned}\right\}. \tag{5.14}$$

Substitute from (5.14), and (5.12) becomes

$$\frac{e}{2mc} \{\overline{(\sigma \,.\, \mathbf{p})\, \psi_{b3}} (\sigma \,.\, \mathrm{A})\, \psi_{a3} + \overline{(\sigma \,.\, \mathbf{p})\, \psi_{b4}} (\sigma \,.\, \mathrm{A})\, \psi_{a4} + \bar{\psi}_{b3} (\sigma \,.\, \mathrm{A}) (\sigma \,.\, \mathbf{p})\, \psi_{a3} + \bar{\psi}_{b4} (\sigma \,.\, \mathrm{A}) (\sigma \,.\, \mathbf{p})\, \psi_{a4}\}$$

$$= \frac{e}{2mc} \Sigma \{\overline{(\sigma \,.\, \mathbf{p})\, \psi_b} (\sigma \,.\, \mathrm{A})\, \psi_a + \bar{\psi}_b (\sigma \,.\, \mathrm{A}) (\sigma \,.\, \mathbf{p})\, \psi_a\} \tag{5.15}$$

approximately. Using Dirac's notation for matrix-components, the first term in the bracket is

$$\sum_{\lambda, \mu, \nu = 1, 2, 3, 4} \overline{(\lambda \,|(\sigma \,.\, \mathbf{p})|\, \mu)\, \psi_{b\mu}} (\lambda \,|(\sigma \,.\, \mathrm{A})|\, \nu)\, \psi_{a\nu}$$

$$= \sum_{\lambda\mu\nu} \bar{\psi}_{b\mu} (\mu \,|(\sigma \,.\, \mathbf{p})|\, \lambda)\, (\lambda \,|(\sigma \,.\, \mathrm{A})|\, \nu)\, \psi_{a\nu}$$

$$= \Sigma\, \bar{\psi}\; (\sigma \,.\, \mathbf{p}) (\sigma \,.\, \mathrm{A})\, \psi_a. \tag{5.16}$$

Thus the matrix-components of (5.10) are approximately the same as those of

$$\frac{e}{2mc}\{(\boldsymbol{\sigma}\,.\,\mathbf{p})(\boldsymbol{\sigma}\,.\,\mathbf{A}) + (\boldsymbol{\sigma}\,.\,\mathbf{A})(\boldsymbol{\sigma}\,.\,\mathbf{p})\}$$

$$= \frac{e}{2mc}\{(\mathbf{p}\,.\,\mathbf{A}) + (\mathbf{A}\,.\,\mathbf{p}) + i\boldsymbol{\sigma}\,.\,[\mathbf{p}, \mathbf{A}] + i\boldsymbol{\sigma}\,.\,[\mathbf{A}, \mathbf{p}]\}$$

$$= \frac{e}{2mc}\{(\mathbf{p}\,.\,\mathbf{A}) + (\mathbf{A}\,.\,\mathbf{p})\} + \frac{eh}{4\pi mc}(\boldsymbol{\sigma}\,.\,\mathrm{curl}\,\mathbf{A}). \qquad (5.17)$$

We have now to calculate the vector potential due to a moving electron. Dirac* has shown that the conservation of electricity is maintained if the density of charge and of current corresponding to a wave-function $\psi$ (with an Hermitian Hamiltonian) are

$$- e\Sigma\,\ddot{\psi}\,\psi \quad \text{and} \quad ec\Sigma\,\bar{\psi}\,\rho'\boldsymbol{\sigma}\psi \qquad (5.20)$$

Thus if we are right in attributing a scalar potential $-e/r$ to the charge on the electron, we should also expect a vector potential due to the moving charge

$$\mathbf{A} = e\rho'\boldsymbol{\sigma}/r. \qquad (5.21)$$

Again, $\rho$ is inconvenient, and it can be removed by the same device as before. It is not necessary to repeat the argument. To a sufficient approximation

$$\mathbf{A} = -\frac{e}{2mc}\left\{(\boldsymbol{\sigma}\,.\,\mathbf{p})\frac{\boldsymbol{\sigma}}{r} + \frac{\boldsymbol{\sigma}}{r}(\boldsymbol{\sigma}\,.\,\mathbf{p})\right\}$$

$$= -\frac{e}{2mc}\left\{\mathbf{p}\frac{1}{r} + \frac{1}{r}\mathbf{p} + i[\boldsymbol{\sigma}, \mathbf{p}]\frac{1}{r} - i\frac{1}{r}[\boldsymbol{\sigma}, \mathbf{p}]\right\}$$

$$= -\frac{e}{2mc}\left\{\mathbf{p}\frac{1}{r} + \frac{1}{r}\mathbf{p}\right\} - \frac{eh}{4\pi mc}\left[\boldsymbol{\sigma}, \nabla\frac{1}{r}\right]. \qquad (5.22)$$

It is interesting to note that just as the last term of (5.17) expresses the energy of a magnet of moment $-\frac{eh}{4\pi mc\,\boldsymbol{\sigma}}$ in the given field, so the last term of (5.22) is the vector potential due to such a magnet. It has not been necessary in producing either of these terms to mention explicitly a magnetic moment of the electron. It appears that *all* its magnetic behaviour can be interpreted in terms of the current due to the charge $-e$ moving with velocity $-c\rho'\boldsymbol{\sigma}$. This current-velocity, whose components have characteristic values $\pm c$, has no connection with the momentum; and conversely $\mathbf{p}$ is fundamentally irrelevant to the electromagnetic field. (5.17) and (5.22) show, however, that the electron's interactions with the field can be represented approximately by means of a current-velocity $\mathbf{p}/m$ and a magnetic moment $-\dfrac{eh}{4\pi mc}\boldsymbol{\sigma}$.*

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* Dirac, 'Roy. Soc. Proc.,' vol. 118, p. 354 (1928).

Substitute from (5.22) in (5.17), inserting suffixes 2 in the former and 1 in the latter, and neglecting terms independent of $\boldsymbol{\sigma}_1$, $\boldsymbol{\sigma}_2$, which are irrelevant to S and constitute an insignificant addition to P;

$$\begin{aligned} \mathrm{S} = & -\frac{e^2h}{8\pi m^2c^2}\left\{\mathbf{p}_1\left[\boldsymbol{\sigma}_2, \nabla_2\frac{1}{r}\right]+\left[\boldsymbol{\sigma}_2, \nabla_2\frac{1}{r}\right]\mathbf{p}_1 - \boldsymbol{\sigma}_1\cdot\left[\mathbf{p}_2, \nabla_1\frac{1}{r}\right]\right. \\ & \left. + \boldsymbol{\sigma}_1\cdot\left[\nabla_1\frac{1}{r}, \mathbf{p}_2\right]\right\} + \left(\frac{eh}{4\pi mc}\right)^2\frac{(\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)-3(\boldsymbol{\sigma}_1\mathbf{r}_0)(\boldsymbol{\sigma}_2\mathbf{r}_0)}{r^3}, \\ = & -\frac{e^2h}{4\pi m^2c^2}\left\{\left[\frac{\mathbf{r}_2-\mathbf{r}_1}{r^3}, \mathbf{p}_2\right]\boldsymbol{\sigma}_1 + \left[\frac{\mathbf{r}_1-\mathbf{r}_2}{r^3}, \mathbf{p}_1\right]\boldsymbol{\sigma}_2\right\} \\ & + \left(\frac{eh}{4\pi mc}\right)^2\frac{(\boldsymbol{\sigma}_1\boldsymbol{\sigma}_2)-3(\boldsymbol{\sigma}_1\mathbf{r}_0)(\boldsymbol{\sigma}_2\mathbf{r}_0)}{r^3}. \end{aligned}$$

This is the same as (5.02). To add the energy of the second electron in the field of the first would be to count the mutual energy twice over. It appears from the above argument that (5.02) is only an approximation, which is convenient when we wish to neglect the smaller components of the wave-functions. Combining (5.10) and (5.21), and adding the electrostatic term, we obtain for the mutual potential energy of two electrons the simple form

$$\frac{e^2}{r}[1-\rho_1'\rho_2'(\boldsymbol{\sigma}_1\cdot\boldsymbol{\sigma}_2)]. \qquad (5.30)$$

(Similarly, the second term of Dirac's Hamiltonian may be interpreted as a kinetic energy

$$-c\rho'(\boldsymbol{\sigma}\cdot\mathbf{p}), \qquad (5.31)$$

since this is the addition to W necessary to balance it. We have called $-c\rho'\boldsymbol{\sigma}$ a "current-velocity," and (5.31) is comparable with the energy of a light-quantum, which is the scalar product of its velocity and its momentum. The electron has also the mass-energy

$$-\rho'''mc^2, \qquad (5.32)$$

which is equivalent to $mc^2$ for the larger components of the wave-functions.)

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* Our approximation does not distinguish between $-\dfrac{eh}{4\pi mc}\boldsymbol{\sigma}$ and $\dfrac{eh}{4\pi mc}\rho'''\boldsymbol{\sigma}$, since $\rho''' = -1$ for the two last components. The latter is required by Darwin's equations (4.1) in 'Roy. Soc. Proc.,' A, vol. 120, p. 627 (1928).

## 6. *The Method of Calculation with One Electron Excited.*

The wave-function for a single electron comprises four functions of position, of which the first two are small, and the other two differ little from solutions of Schrödinger's equation. Provided that the spin-energy S is thrown into a suitable form, it is sufficiently accurate to take as the two wave-functions corresponding to an $(n, k, u)$ orbit

$$\left.\begin{aligned} \psi_{-k-1}{}^{u} &= 0,\ 0,\ (k+u+1)\,\mathrm{P}_k{}^{u} g_{nk},\ (-k+u)\,\mathrm{P}_k{}^{u+1} g_{nk} \\ \psi_k{}^{u} &= 0,\ 0 \qquad\qquad \mathrm{P}_k{}^{u} g_{nk} \qquad\qquad \mathrm{P}_k{}^{u+1} g_{nk} \end{aligned}\right\} \tag{6.0}$$

where $\mathrm{P}_k{}^u$ is defined in Darwin's manner, and $g_{nk}$ is the radial part of the solution of Schrödinger's equation. (The lower suffix of $\psi$ is Dirac's $j$.) Thus

$$\left.\begin{aligned} \psi_{-k-1}{}^{u} + (k-u)\,\psi_k{}^{u} &= \phi_k{}^{u}\chi_a \\ -\,\psi_{-k-1}{}^{u} + (k+u+1)\,\psi_k{}^{u} &= \phi_k{}^{u+1}\chi_b \end{aligned}\right\} \tag{6.1}$$

where

$$\phi_k{}^{u} = (2k+1)\,\mathrm{P}_k{}^{u} g_{nk}, \tag{6.2}$$

and $\chi_a$, $\chi_b$ are functions of the spin co-ordinate only, with components

$$\left.\begin{aligned} \chi_a &= 0,\ 0,\ 1,\ 0 \\ \chi_b &= 0,\ 0,\ 0,\ 1 \end{aligned}\right\} \tag{6.3}$$

For states in which only one electron is excited, a group of four wave-functions such as are deduced by Heisenberg as first approximations to the complete wave-functions is

$$\left.\begin{aligned} \psi_\alpha &= [\phi_0{}^0(1)\,\phi_k{}^{u+1}(2) - \phi_0{}^0(2)\,\phi_k{}^{u+1}(1)]\,\chi_b(1)\,\chi_b(2) \\ \psi_\beta &= [\phi_0{}^0(1)\,\phi_k{}^{u-1}(2) - \phi_0{}^0(2)\,\phi_k{}^{u-1}(1)]\,\chi_a(1)\,\chi_a(2) \\ \psi_\gamma &= [\phi_0{}^0(1)\,\phi_k{}^{u}(2) - \phi_0{}^0(2)\,\phi_k{}^{u}(1)]\,[\chi_a(1)\,\chi_b(2) + \chi_b(1)\,\chi_a(2)] \\ \psi_{\mathrm{IV}} &= [\phi_0{}^0(1)\,\phi_k{}^{u}(2) + \phi_0{}^0(2)\,\phi_k{}^{u}(1)]\,[\chi_a(1)\,\chi_b(2) - \chi_b(1)\,\chi_a(2)] \end{aligned}\right\} . \tag{6.4}$$

Of these the first three have the same energy $\mathrm{E} + \Delta\mathrm{E}^{\mathrm{I}}$, and are not true first approximations, but must be taken in linear combinations to form $\psi_{\mathrm{I}}$, $\psi_{\mathrm{II}}$, $\psi_{\mathrm{III}}$.

The functions in (6.4) are chosen so that by means of (6.1) they can all be expressed in terms of the four $\psi_m$'s

$$\left.\begin{aligned} \psi_1 &= \psi_{-1}{}^{0}(1)\,\psi_{-k-1}{}^{u-1}(2) - \psi_{-1}{}^{0}(2)\,\psi_{-k-1}{}^{u-1}(1) \\ \psi_2 &= \psi_{-1}{}^{0}(1)\,\psi_k{}^{u-1}(2) - \psi_{-1}{}^{0}(2)\,\psi_k{}^{u-1}(1) \\ \psi_3 &= \psi_{-1}{}^{-1}(1)\,\psi_{-k-1}{}^{u}(2) - \psi_{-1}{}^{-1}(2)\,\psi_{-k-1}{}^{u}(1) \\ \psi_4 &= \psi_{-1}{}^{-1}(1)\,\psi_k{}^{u}(2) - \psi_{-1}{}^{-1}(2)\,\psi_k{}^{u}(1) \end{aligned}\right\} \tag{6.5}$$

In each of these functions the sum of the magnetic quantum numbers is the same, $u - 1$ pairing with 0 and $u$ with $-1$. The set of functions (6.4) can be remembered by supposing that $\chi_a$, $\chi_b$ contribute $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively to the magnetic quantum number, which defines the total angular momentum about the $z$-axis. This corresponds to Dirac's equation

$$\mathbf{M} = \mathbf{m} + \tfrac{1}{2} h \boldsymbol{\sigma}, \tag{6.6}$$

and the fact that $\sigma_z$ behaves like $+1$ with $\chi_a$ and $-1$ with $\chi_b$ (see equation (6.8) below). It appears during the course of the calculations that this set of functions remains separate when the perturbation by S is applied, so that the degeneracy in $u$ causes no embarrassment.

Evidently $\delta E_1 = \delta E_3$, $\delta E_2 = \delta E_4$, and $\delta E_1 - \delta E_2$ is the spin-doublet separation for the $(nk)$-orbit.

The calculation of $S_{mm'}$, etc., will only be described shortly here. Since the relations between the $\psi_m$'s and $\psi_\alpha$, $\psi_\beta$, $\psi_\gamma$, $\psi_{IV}$ are known, it is convenient to calculate first such integrals as

$$S_{aa} = \int \bar{\psi}_a S \psi_a \tag{6.7}$$

The summation with respect to the spin co-ordinates is carried out with the help of the formulæ

$$\left.\begin{array}{lll} \sigma_x \chi_a = \chi_b, & \sigma_y \chi_a = i\chi_b, & \sigma_z \chi_a = \chi_a \\ \sigma_x \chi_b = \chi_a, & \sigma_y \chi_b = -i\chi_a, & \sigma_z \chi_b = -\chi_b \end{array}\right\}. \tag{6.8}$$

In the sextuple integral the integrations with respect to the angular variables can be performed, leaving only radial integrals. From $S_{aa}$, etc., the $S_{mm'}$'s are found and substituted in (4.23). This equation can then be solved to give the triplet separations.

The radial integrations require a knowledge of $g_{10}$ and $g_{nk}$. Rough approximations to these functions have been used, with certain simplifications suitable to widely separated orbits.

## 7. *Numerical Results.*

The result of the calculations described above is

$$\left.\begin{array}{l} \delta E^{I} - \delta E^{II} = \dfrac{mc^2 (Z-1)^3 \gamma^4}{n^3 k (2k+1)} \left\{ \dfrac{Z-3}{2} + \dfrac{3}{2k+3} \right\} \\[2ex] \delta E^{II} - \delta E^{III} = \dfrac{mc^2 (Z-1)^3 \gamma^4}{n^3 (k+1)(2k+1)} \left\{ \dfrac{Z-3}{2} - \dfrac{3}{2k-1} \right\} \end{array}\right\}. \tag{7.0}$$

where $Ze$ is the nuclear charge, $\gamma$ the fine structure constant $2\pi e^2/ch$.

The following table shows the ratio $\delta E^{I} - \delta E^{II} : \delta E^{II} - \delta E^{III}$ with the sign of each separation, for the P- and D-terms in the cases $Z = 2$ (He), $Z = 3$ ($Li^+$) and $Z \rightarrow \infty$ (normal triplet).

$$\left.\begin{array}{cccc} Z & 2 & 3 & \infty \\ k = 1 & 2 : -35 & 2 : -5 & 2 : 1 \\ k = 2 & -1 : -14 & 9 : -14 & 3 : 2 \end{array}\right\}. \tag{7.1}$$

When $n$ is small some of the approximations used are unsuitable. A more accurate calculation for the $2^3P$ terms of He gives

$$\left.\begin{array}{l} \delta E^{I} - \delta E^{II} = -0\cdot003\,\dfrac{\Upsilon^2 e^2}{a} \\ \delta E^{II} - \delta E^{III} = -0\cdot063\,\dfrac{\Upsilon^2 e^2}{a} \end{array}\right\}, \tag{7.2}$$

where $a$ is the radius of the first hydrogen orbit. This is a completely inverted triplet with two very close components. The ratio of its separations is very sensitive to small errors in the theory, and (7.2) is in sufficient accord with the experiments of Hansen* and of Houston† who find $\delta E^{II} - \delta E^{III} : \delta E^{I} - \delta E^{II}$ is about 13 or 14. For 3D Houston gives a partly inverted triplet with separations $0\cdot02$ cm.$^{-1}$ and $0\cdot06$ cm.$^{-1}$, which agrees neither with this theory nor with Heisenberg's.

The magnitude of the separation of the extreme components of He $2^3P$ is given by (7.2) as $0\cdot77$ cm.$^{-1}$ as compared with Heisenberg's $0\cdot62$ cm.$^{-1}$ and the observed value of $1\cdot06$ cm.$^{-1}$. Sugiura,‡ by using more accurate wave-functions has raised Heisenberg's result to $0\cdot86$ cm.$^{-1}$, and a similar correction would improve our value.

For other helium triplets the following extreme separations are found from (7.0) :—

$$\left.\begin{array}{lccc} & 3P & 3D & 4D \\ \delta\nu \text{ (calc.), cm.}^{-1} \ldots\ldots & 0\cdot25 & 0\cdot046 & 0\cdot02 \\ \delta\nu \text{ (Houston), cm.}^{-1} \ldots & 0\cdot286 & 0\cdot08 & 0\cdot04 \end{array}\right\}. \tag{7.3}$$

The calculated values are uncorrected, but no correction is likely to produce Houston's observed values for the D triplets.

The probabilities of ortho-para transitions have been estimated as explained in the perturbation theory. We give two results for the ratio $X_{\mathrm{II}\,0}{}^2/C_{\mathrm{II}} : X_{\mathrm{IV}\,0}{}^2/C_{\mathrm{IV}}$. $X_{\mathrm{I}\,0}$ and $X_{\mathrm{III}\,0}$ vanish to our order of approximation.

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* Hansen, 'Nature,' vol. 119, p. 237 (1927).

† Houston, 'Proc. Nat. Acad. Sci.,' vol. 13, p. 91 (1927).

‡ Sugiura, 'Z. f. Physik,' vol. 44, p. 190 (1927).

$$\left.\begin{array}{cc} \text{He, } 1S - 2P & \text{Li}^+\text{, } 1S - 2P \\ 10^{-7} & 7\,.\,10^{-7} \end{array}\right\} . \qquad (7.4)$$

Thus the line $2\,{}^3P_1 - 1\,{}^1S_0$ should be $10^{-7}$ as intense as the line $2\,{}^1P_1 - 1\,{}^1S_0$ in helium. Such lines are not observed.

The above ratio of intensities is roughly $\frac{7}{8}\,(\delta\nu/\Delta\nu)^2$, where $\Delta\nu$ is the ortho-para separation. This formula may give the right order of magnitude for other atoms with two series electrons. The following table shows the ratio so calculated of the intensities of $m\,{}^3P_1 - 1\,{}^1S_0$ and $m\,{}^1P_1 - 1\,{}^1S_0$, for observed intercombinations.[*]

| Element. | *m.* | Ratio 1 in | Element. | *m.* | Ratio 1 in |
|---|---|---|---|---|---|
| Mg | 1 | 200000 | Zn | 1 | 2500 |
| Ca | 1 | 12000 | | 2 | 1800 |
| | 2 | 160 | Cd | 1 | 260 |
| Sr | 1 | 700 | | 2 | 150 |
| Ba | 1 | 85 | | 3 | 100 |
| | 2 | 220 | Hg | 1 | 22 |

(7.5)

The second intercombination line of Hg is omitted, since $\delta\nu > \Delta\nu$ and the approximation becomes absurd; the first line is well known to be intense.

[*Added December* 13, 1928.—Two of the ratios tabulated above are in fair agreement with experimental data due to Kuhn.[†] He measures intensities by a quantity $f$, given by

$$f = Bmh\nu/\pi c^2.$$

The Einstein B-coefficient is proportional to the square of the matrix-component of the electric moment, so that the ratios tabulated in (7.5) are ratios of $f\lambda$. We quote Kuhn's observations for three lines, with Fowler's notation and wave-lengths.

| | | | |
|---|---|---|---|
| Cd ........ | $1\,{}^1S - 1\,{}^3P_1$ | $\lambda = 3261$ | $f = 1{\cdot}9\,.\,10^{-3}$ |
| | $1\,{}^1S - 1\,{}^1P$ | $\lambda = 2288$ | $f = 1{\cdot}20$ |
| Hg ...... | $1\,{}^1S - 1\,{}^3P_1$ | $\lambda = 2537$ | $f = 2{\cdot}5\,.\,10^{-2}$ |

No value of $f$ is given for Hg $1\,{}^1S - 1\,{}^1P$ ($\lambda = 1850$); a reasonable estimate is about 1·25. The observed ratio of $f\lambda$ for the Cd lines is 1/440 (*cf.* 1/260), and for the Hg lines about 1/37 (*cf.* 1/22).]

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[*] Data from A. Fowler, 'Report on Series in Line Spectra' (1922).

[†] Kuhn, 'Danske Vidensk. Selskab.,' vol. 7, §12, pp. 23, 85 (1926)

## 8. *Classification and Selection Rules.*

The form for large Z of the spin energies quoted above suggests that the three terms, I, II, III, correspond respectively to $j = k + 1,\ k,\ k - 1$. It is easy to verify that their weights are $2k + 3,\ 2k + 1,\ 2k - 1$. The group of four wave-functions (6.4) exists for $k \geqslant 1$, $|u| < k$. If, however, $|u| = k$, $\psi_\alpha$ or $\psi_\beta$ drops out, and the spin energies of the two remaining ortho-terms are found to be $\delta E^{I}$ and $\delta E^{II}$. If $|u| = k + 1$, only one function survives, and its spin energy is $\delta E^{I}$. So the weights of the ortho-terms are as stated, and that of the para-term is $2k + 1$, *i.e.*, $j = k$. $k = 0$ is a special case. $u = \pm 1$ gives a single ortho-term as before, with spin energy $\delta E_1$. For $u = 0$ the group consists of $\psi_\gamma$ and $\psi_{IV}$, and the former again has spin energy $\delta E_1$. We thus have the familiar ${}^3S_1$ and ${}^1S_0$, with weights 3 and 1 respectively.

The approximate wave-functions for the ortho-terms are found in the course of the theory. They are :—

$$\left.\begin{aligned}
\psi_{I} &= (k - u + 1)(k - u)\,\psi_\alpha + (k + u + 1)(k + u)\,\psi_\beta \\
&\qquad\qquad - (k + u + 1)(k - u + 1)\,\psi_\gamma \\
\psi_{II} &= -(k - u)\,\psi_\alpha + (k + u)\,\psi_\beta + u\psi_\gamma \\
\psi_{III} &= \psi_\alpha + \psi_\beta + \psi_\gamma
\end{aligned}\right\} \qquad (8.0)$$

From these we can calculate matrix-components of the electric moment of the atom for various transitions between ortho-states. They are found to vanish unless $\Delta k = \pm 1$, $\Delta j = 0$ or $\pm 1$, thus verifying the selection rules. On taking the squares of the matrix-components to represent the intensities of the corresponding lines, the summation rules are also verified (approximately) inside the triplets.

## 9. *A Triplet of Doubly Ionised Oxygen.*

So far, one electron has been confined to an orbit for which $k = 0$. The next simplest case is perhaps that in which both electrons are in $(n, 1)$ orbits. This is the situation for those terms of $O^{++}$ and $N^{+}$ which give rise to lines in the spectra of the nebulæ, if we treat the complete K and $L_1$ shells as forming a core in whose central field the two series electrons move.

In this case there are in all 15 wave-functions, arranged in groups comparable with (6.4), which may be given total magnetic quantum numbers $u$ as follows :—

$$\left.\begin{array}{lcrrrrr}
u & = & -2 & -1 & 0 & 1 & 2 \\
A & & 1 & 2 & 3 & 2 & 1 \\
S & & 1 & 1 & 2 & 1 & 1
\end{array}\right\} \qquad (9.0)$$

Opposite A is the number of wave-functions in the group which are antisymmetrical in the position coordinates, and so give ortho-terms. Opposite S is the number of symmetrical functions.

One of the para-terms for $u = 0$ has the same energy as all the para-terms in the other groups; so it has weight 5 and is ${}^1D_2$. The other para-term is ${}^1S_0$. The ortho-terms arrange themselves as before into ${}^3P'_{012}$.

The triplets are nearly "normal"; the ratio of the separations ${}^3P'_2 - {}^3P'_1 : {}^3P'_1 - {}^3P'_0$ is found to be approximately

$$2Z' - \tfrac{21}{80} : Z' + \tfrac{7}{32}. \tag{9.1}$$

Here $Z'e$ is some sort of effective nuclear charge, allowing for screening by the K and $L_I$ shells. (9.1) gives the observed ratio* for $O^{++}$ with $Z'$ between 4 and 5, which is reasonable. It is a puzzling circumstance, however, that the observations† on the ions $O^{++}$, $N^+$, C, give greater values to the above ratio for the smaller atomic numbers, instead of the reverse.

It had been hoped that some new system of classification or new selection rules might appear from the new theory to account for the nebular lines. These seem to be due to transitions such as ${}^3P'_2 - {}^1D_2$, ${}^3P'_1 - {}^1D_2$ and ${}^1D_2 - {}^1S_0$. The first two are para-ortho transitions, and might be treated in the same way as such transitions in helium. This, however, would express their intensities as small fractions of the intensities of combinations within ${}^3P'$ which are themselves "forbidden" since the $k$ of neither electron alters. It should be emphasised that such lines are not completely excluded by the theory, which only predicts that they are normally extremely weak. To estimate the probabilities of the transitions involved it would be necessary to proceed to higher orders of the perturbation by P. This makes ${}^3P'_2 - {}^3P'_1$, etc., possible by adding to the approximate wave-functions small wave-functions with different $k$'s. The probability would be of the order of $(\Delta E)^2$ as compared with a line obeying the selection rules; and we should expect the intercombination lines to be weaker still in a ratio of the order of $(\delta E/\Delta E)^2$. Their prominence in the nebular spectra must therefore be due to the special conditions of the gas which emits them.

The detailed account‡ of this work has an appendix containing formulæ for certain integrals of the type

$$\int_{-1}^{1} P_l^u(\mu)\, P_m^v(\mu)\, P_n^w(\mu)\, d\mu \qquad (u = v + w).$$

Such integrals occur in the calculation of $S_{aa}$, etc.

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* A. Fowler, 'Roy. Soc. Proc.,' A, vol. 117, p. 321 (1927).

† ($N^+$) Bowen, 'Phys. Rev.,' vol. 29, p. 231 (1927); (C) A. Fowler and Selwyn, 'Roy. Soc. Proc.,' A, vol. 118, p. 34 (1928).

‡ 'Phil. Trans.,' A. vol. 228, p. 151 (1929).

# *Skin Effect in Rectangular Conductors at High Frequencies.*

By J. D. Cockcroft, Ph.D.

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## 1. *Introduction.*

There is at present little exact information either theoretical or experimental on the high frequency resistance of cylindrical conductors of rectangular section, although the general nature of the phenomenon is quite well known and has been exhaustively treated in the case of circular conductors by Kelvin, Heaviside, Russell and others.*

The first method of attack on the problem of the rectangular conductor is to treat it as a strip of infinite breadth when the problem becomes one dimensional and requires simply a solution of

$$\frac{\partial^2 E}{\partial x^2} = \frac{4\pi\mu}{\rho}\frac{\partial E}{\partial t}$$

E being the electrical force and $\mu$ and $\rho$ the permeability and resistivity respectively. The solution of the problem for two parallel strips was first given by Rayleigh† and it was shown that for high frequencies the current decreases exponentially toward the centre of the conductor, being confined effectively to a surface layer so that the resistance of the conductor was the same as if composed of surface strips of thickness $(2\pi\mu\omega/\rho)^{-\frac{1}{2}}$, $\omega$ being the periodicity. This approximation, however, gives much too low values for the high frequency resistance of a conductor of finite breadth.

The problem of the conductor of rectangular section was discussed by Heaviside‡ and compared with the problems arising in the St. Venant theory of torsion for the case when the return conductor is a closely fitting sheath. In this case the current distribution is uniform round the boundary of the conductor and a simple solution is possible in a series of trigonometrical and hyperbolic terms. This solution was recently given by Strutt§ but it has little practical importance since the return conductor is never of this form and current distribution is in general far from uniform round the boundary.

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* Kelvin, 'Math. and Phys. Papers,' vol. 5, p. 491; Heaviside, 'Electrical Papers, vol. 1, pp. 353, 429; Russell, 'Theory of Alternating Currents,' vol. 1, pp. 46, 367.

† 'Scientific Papers,' vol. 2, p. 496.

‡ 'Electrical Papers,' vol. 2.

§ 'Ann. Physik,' vol. 83, p. 979 (1927).

An alternative method of attack is to treat the conductor as an ellipse of large eccentricity when as was pointed out by Strutt,[*] a solution is possible in terms of Mathieu functions, although an actual numerical solution was not obtained. For low frequencies therefore no solution exists at present which can be used to give numerical results. At higher frequencies the problem becomes much simplified since, as was pointed out by Kelvin (*loc. cit.*) the surface of the conductor becomes a stream line in the magnetic field and the problem of the distribution of field becomes analogous to an electrostatic problem, magnetic stream lines replacing equipotential surfaces and the current density corresponding to the electrostatic surface density. This analogy was used by Butterworth[†] to calculate the effective resistance of two parallel cylinders of circular section at high frequencies and has lately been used by Strutt[‡] to find the resistance of an isolated cylinder of elliptical section as an approximation to the rectangular conductor.

The method may, however, be applied equally well to the rectangular conductor since it is possible to calculate the electrostatic field outside an isolated cylindrical conductor of rectangular section using the method of the Schwartz-Christoffel transformation, first formally applied to this type of problem by Michel.[§] The solution of this electrostatic problem extended to include the use of curved edges, was recently obtained by the writer in a form suitable for numerical computations[||] and field distributions worked out for a number of actual cases. This solution is applied here to the skin effect problem and the results compared with the results for the ellipse and with such experimental data as is available.

## 2. *The General Relation between the Alternating Current Resistance of a Cylindrical Conductor and the Electrostatic Problem.*

Let $\sigma$ be the surface density of electrification of the cylinder in the electrostatic problem. It will then represent the time maximum of the surface current density or $1/4\pi$ times the tangential magnetic field at the surface in the skin effect problem. We have already stated that the "effective depth of penetration" of current into the conductor is given for infinite plane surfaces by $1/m$ where $m = (2\pi\mu\omega/\rho)^{\frac{1}{2}}$. This relation will hold for cylindrical conductors of any shape provided the radius of curvature of the boundary surface is small compared with $1/m$. The dissipation of energy per unit length of conductor and circumferential dimensions $ds$ will then be $\frac{1}{2}m\rho\sigma^2 ds$ and the total dissipation per unit length will be $\frac{1}{2}m\rho\int\sigma^2 ds$, the integral being taken round the surface of the conductor. This must equal $\frac{1}{2}\mathrm{I}^2\mathrm{R}$ if I be the maximum value of the total current and R the alternating current resistance so that

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[*] 'Ann. Physik,' vol. 84, p. 485 (1927).

[†] 'Roy. Soc. Proc.,' A, vol. 107, p. 707 (1925).

[‡] 'Ann. Physik,' vol. 85, p. 781 (1928).

[§] 'Phil. Trans.,' vol. 181, p. 389 (1890).

[||] 'J. Inst. Elec. Eng.,' vol. 66, p. 400 (1928).

$$\mathrm{R} = \frac{m\rho}{\mathrm{I}^2}\int\sigma^2 ds.$$

We have also $\mathrm{I} = \int\sigma ds$ so that

$$\mathrm{R} = m\rho\int\sigma^2 ds \Big/ \left\{\int\sigma ds\right\}^2. \tag{1}$$

As a check on this result, we note that for an isolated cylindrical conductor of circular section, $\sigma$ is constant over the surface, so that

$$\mathrm{R} = m\rho/2\pi r = (\omega\mathrm{R}_0/2)^{\frac{1}{2}},$$

a well-known result.

### 3. *The Alternating Current Resistance of an Isolated Conductor of Rectangular Section.*

The distribution of electrostatic stress round the cylindrical conductor of

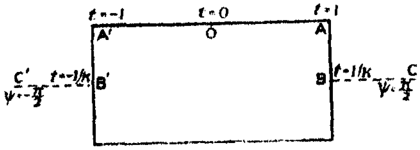

Fig. 1.

fig. 1 is obtained by the method of the Schwartz-Christoffel transformation using the transformations

$$\frac{dz}{dt} = \sqrt{(t^2-1)(t^2-1/\kappa^2)}, \quad \frac{dw}{dt} = (t^2-1/\kappa^2)^{-\frac{1}{2}}. \tag{2}$$

The upper half of the plane of $t$ being transformed into that part of the plane of $z$ bounded internally by the flux lines BC, B′C′ and the upper surface of the conductor BAO A′B′.

$w = \phi + j\psi$ gives the field in the $t$ plane, $\phi$ being the potential function, and $\psi$ the flux function. The electrostatic stress in the $z$ plane is given by

$$|dw\,|\,dz| = 1/\sqrt{(t^2-1)},$$

so that the surface density $\sigma$ is $1/4\pi\sqrt{(t^2-1)}$ and

$$\int \sigma^2\,ds = \frac{1}{4\pi^2}\int_0^{1/\kappa} \frac{dt}{\sqrt{(t^2-1)(t^2-1/\kappa^2)}},$$

the substitution $t = \operatorname{sn} u$ leading to

$$\int \sigma^2\,ds = \kappa(\mathrm{F}+\mathrm{F}')/4\pi^2.$$

F and F′ being the complete elliptic integrals of the first kind to moduli $\kappa$ and $\kappa_1 = \sqrt{(1-\kappa^2)}$.

We have also

$$\int \sigma\,ds = \frac{1}{\pi}\int_0^{1/\kappa} \frac{dt}{\sqrt{(1/\kappa^2-t^2)}} = \tfrac{1}{2},$$

so that

$$\int \sigma^2\,ds \Big/ \left\{\int \sigma\,ds\right\}^2 = \kappa(\mathrm{F}+\mathrm{F}')/\pi^2. \tag{3}$$

We have further for the conductor shape

$$\mathrm{OA} = a = (\mathrm{E}-\kappa_1{}^2\mathrm{F})/\kappa \tag{4}$$

$$\mathrm{AB} = b = (\mathrm{E}'-\kappa^2\mathrm{F}')/\kappa, \tag{5}$$

E and E′ being the complete elliptic integrals of the second kind to moduli $\kappa$ and $\kappa_1$ respectively.

We have then from (1)

$$\mathrm{R}/\mathrm{R}_0 = \kappa\,(\mathrm{F}+\mathrm{F}')\sqrt{(2\pi\rho\omega)}/\pi^2\mathrm{R}_0,$$

and substituting $\mathrm{R}_0 = \rho/4ab$ we have

$$\begin{aligned}\mathrm{R}/\mathrm{R}_0 &= 2\pi^{-\frac{3}{2}}(\mathrm{E}-\kappa_1{}^2\mathrm{F})^{\frac{1}{2}}(\mathrm{E}'-\kappa^2\mathrm{F}')^{\frac{1}{2}}(\mathrm{F}+\mathrm{F}')(2\omega/\mathrm{R}_0)^{\frac{1}{2}},\\ &= f(b/a)\sqrt{(2\omega/\mathrm{R}_0)}/\pi,\end{aligned} \tag{6}$$

since $\mathrm{R}/\mathrm{R}_0$ is a function of $\kappa$ only and therefore from (4) and (5) of the shape factor $b/a$.

In fig. 2 we plot $f(b/a)$ for shape factors of one to two hundred.

For the ellipse, Strutt (*loc. cit.*) obtained

$$\mathrm{R}_e/\mathrm{R}_0 = \mathrm{F}(1-a^2/b^2)^{\frac{1}{2}}(a/b)^{\frac{1}{2}}\pi^{-1}\sqrt{(2\omega/\mathrm{R}_0)} = f_e(b/a)\pi^{-1}\sqrt{(2\omega/\mathrm{R}_0)}, \tag{7}$$

F denoting the complete elliptic integral of the first kind. On fig. 2 we plot for comparison $f_e(b/a)$ and see that for values of $b/a$ about 40 the two curves give equal values but for large ratios of $b/a$ the ellipse gives larger values.

For large values of $b/a$ or small $\kappa$, we obtain from (4), (5) and (6) $a/b = \pi\kappa^2/4$ and

$$\begin{aligned}\mathrm{R}/\mathrm{R}_0 &= \pi^{-\frac{3}{2}}(a/b)^{\frac{1}{2}}\log_e(4\pi b/a)(2\omega/\mathrm{R}_0)^{\frac{1}{2}}\\ &= \pi^{-\frac{1}{2}}(\mathrm{R}_e/\mathrm{R}_0).\end{aligned} \tag{8}$$

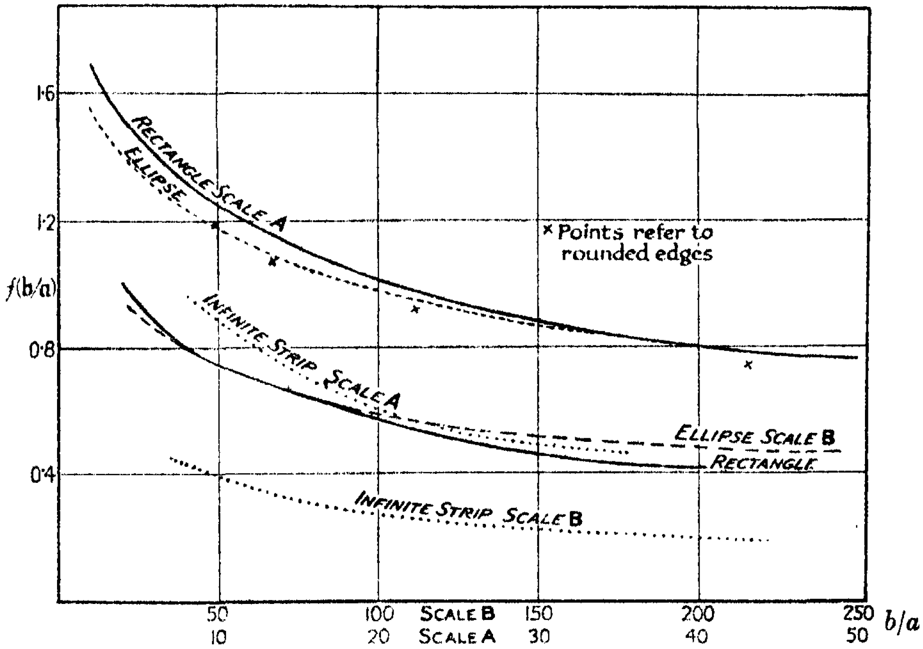

Fig. 2.

If we were to treat the rectangle as part of an infinite strip, we should obtain

$$R/R_0 = (\pi a/b)^{\frac{1}{2}}(\omega/2R_0)^{\frac{1}{2}}. \tag{9}$$

The points obtained for this expression are also plotted on fig. 2 and it is seen that the values obtained are much lower than for the ellipse. It is also obvious from (8) and (9) that the two expressions will not tend to equality for large values of $b/a$.

### 4. *Correction for Curvature of the Edges.*

Since we have stated that the method used is only justifiable provided the curvature of the surface is at all points small compared with $1/m$ it is necessary to satisfy ourselves that taking the edges to be ideally sharp has not introduced an error. The solution of the electrostatic problem for the case of curved edges has been given by the writer (*loc. cit.*) and we take over the results to find

$$R/R_0 = \frac{2}{\pi^{\frac{1}{2}}}\left(\frac{2\omega}{R_0}\right)^{\frac{1}{2}}\frac{1}{(\kappa'^2-\kappa^2)}(P+Q)^{\frac{1}{2}}(P'+Q')^{\frac{1}{2}}[P-P'+Q'-Q-(r_1+r_2)$$
$$+(\text{arc sin }\kappa'-\text{arc sin }\kappa)(\kappa'^2-\kappa^2)], \tag{10}$$

$$=f(b/a)\frac{1}{\pi}\sqrt{(2\omega/R_0)},$$

where

$$P = E(\pi/2, \kappa) - \kappa_1^2 F(\pi/2, \kappa), \qquad P' = E(\pi/2, \kappa_1) - \kappa^2 F(\pi/2, \kappa_1),$$

$$Q = E(\pi/2, \kappa') - \kappa_1'^2 F(\pi/2, \kappa'), \qquad Q' = E(\pi/2, \kappa_1') - \kappa'^2 F(\pi/2, \kappa_1'),$$

$$OB = a = P + Q, \ OE = b = P' + Q', \tag{11}$$

$$r_1 = OC = \{E(\pi/2, \kappa') - E(\beta, \kappa')\} + \kappa_1'^2 \{F(\pi/2, \kappa') - F(\beta, \kappa')\},$$

$$r_2 = OD = \{E(\pi/2, \kappa_1) - E(\beta', \kappa_1)\} + \kappa^2 \{F(\pi/2, \kappa_1) - F(\beta', \kappa_1)\},$$

$$\sin \beta = \kappa/\kappa'. \qquad \sin \beta' = \kappa_1'/\kappa_1,$$

$$\kappa_1 = (1 - \kappa^2)^{\frac{1}{2}}, \qquad \kappa_1' = (1 - \kappa'^2)^{\frac{1}{2}}.$$

The dimensions of the conductor are shown in fig. 3. The curve obtained for the corners does not differ by much from a circular arc, the dimensions $r_1$ and $r_2$ differing in practice only by a few per cent. Variation of the two moduli $\kappa$ and $\kappa'$ gives a series of conductor dimensions with different radii and ratios $a/b$.

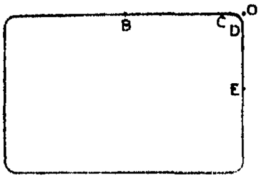

Fig. 3.

From (10), values of $R/R_0$ were calculated for a series of conductors for which $2a/(r_1 + r_2)$ was approximately 10 and $b/a$ varied from 9·7 to 43. The points obtained are marked on fig. 2. It is seen that they give about 5 per cent. lower resistance ratios than for sharp edges. This is, of course, due to the diminution of current density at the edges obtained by rounding them to a small radius. It is clear, therefore, that we make no serious error in taking the edges to be sharp for very high frequencies.

### 5. *Proximity Effects.*

The effect of a parallel return conductor in changing the effective resistance of the conductor at high frequencies could be investigated exactly if the solution of the electrostatic problem of two charged rectangles with parallel sides as shown in fig. 4 was known.

Actually the solution involves intractable integrals and it is only possible to approximate by using the solution for the case when one of the dimensions is semi-infinite as in fig. 5.

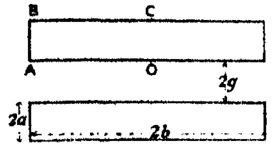

Fig. 4.

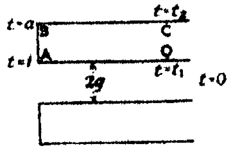

Fig. 5.

If the spacing distance $2g$ is less than one-quarter of the dimensions $2a$, then towards the centres of the opposing faces the stress distribution will be practically uniform and equal to that at the corresponding distance from the corner of the semi-infinite conductor. Towards the point C on the other hand the stress will fall to very small values and will again differ little from that of the semi-infinite case.

The appropriate transformations for the solution of the electrostatic problem of fig. 5 were first given by Kirchoff* and are

$$\frac{dz}{dt} = \frac{\sqrt{(t-a)(t-1)}}{t}, \qquad \frac{dw}{dt} = \frac{1}{t},$$

so that

$$\frac{dw}{dz} = 1/\sqrt{(t-a)(t-1)},$$

and

$$16\pi^2 \int \sigma^2 ds = a^{\frac{1}{2}} \left[\log \frac{2a - (a+1)t - 2(a\lambda)^{\frac{1}{2}}}{t}\right]_{t_2}^{t_1},$$

$$4\pi \int \sigma\, ds = \log t_2/t_1, \qquad \lambda = \sqrt{(t-a)(t-1)}.$$

The relative conductor dimensions are given by

$$t/g = \{1 - (a+1)/2\sqrt{(a)}\} \tag{12}$$

$$\begin{aligned} \text{OA} = a^{\frac{1}{2}} \log \frac{2a - (a+1)t_1 - 2\,.\,(a\lambda)^{\frac{1}{2}}}{a-1} \\ - \frac{(a+1)}{4} \log \frac{(a+1) + 2\lambda^{\frac{1}{2}} - 2t_1}{a+1-2\lambda^{\frac{1}{2}} - 2t_1} - a^{\frac{1}{2}} \log t_1 - \lambda^{\frac{1}{2}}. \end{aligned} \tag{13}$$

$$\begin{aligned} \text{CD} = a^{\frac{1}{2}} \log t_2 - a^{\frac{1}{2}} \log \frac{(a+1)t_2 - 2a - 2(a\lambda)^{\frac{1}{2}}}{(a-1)} + \lambda^{\frac{1}{2}} \\ - \frac{(a+1)}{2} \operatorname{arc\,cosh} \frac{2t_2 - (a+1)}{a-1}. \end{aligned} \tag{14}$$

From (12), (13) and (14) $a$, $t_1$ and $t_2$ can easily be chosen to give desired conductor dimensions. $R/R_0$ was calculated for values of $t/g$ of 0·25, 0·45 and 1·6 and values of $b/a$ ranging from 20 to 230. The results are plotted on fig. 6 with the curve for the isolated conductor as a comparison. It is seen that the points do not differ much from those for the isolated conductor. For the largest values of $t/g$ they actually show a decrease in the effective resistance, increasing again for closer spacing. It is unfortunately not legitimate to apply the calculation to conductors of larger spacing as the approximations become inaccurate. It is not possible therefore to say for what spacing the minimum resistance is obtained. The diminution in resistance is obviously due to the fact that the current density becomes practically uniform along the face OA and decreases along the face BC.

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* 'Gesammelte Abhandlungen,' p. 101.

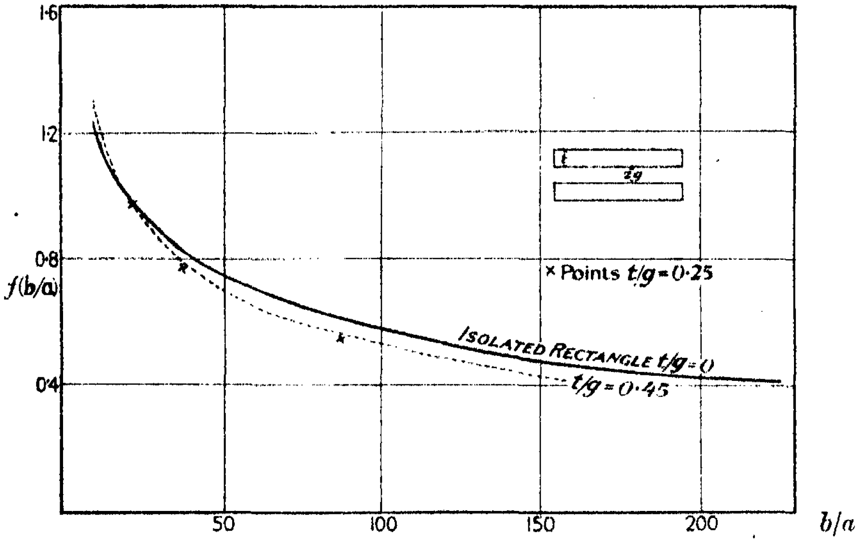

Fig. 6.

### 6. *Range of Validity of Results and Comparison with Experiments.*

The results have shown that we may express the resistance ratio for infinite frequencies in the form $R/R_0 = f(a/b)\,\frac{1}{\pi}\,\sqrt{(2\omega/R_0)}$. For low frequencies $R/R_0$ obviously follows a different law so that for intermediate frequencies we must have

$$R/R_0 = A + f(a/b)\,\frac{1}{\pi}\,\sqrt{(2\omega/R_0)}, \tag{15}$$

the constant A having to be determined by experiment for different conductor shapes until such time as a solution for the low frequencies is found.

The range of frequencies within which (15) may be expected to hold rigidly is fixed by the consideration that the "effective depth of penetration," $1/m$ must be smaller than any of the conductor dimensions $a$, $b$ or $r$. Actually however we shall probably be able to apply the results for smaller values of $r$ than is allowed by this rule without making errors which will be serious in practice. Table I gives values of $1/m$ for different frequencies for copper.

Table I.

| | 50. | 500. | 5000. | $10^5$, | $5 \cdot 10^5$. | $5 \cdot 10^6$. |
|---|---|---|---|---|---|---|
| $1/m$ (mm.) ...................... | 9·33 | 2·95 | 0·933 | 0·209 | 0·0933 | 0·0295 |

The only experimental results on the high frequency resistance of rectangular conductors are given in papers by Kennelly, Laws and Pierce,* and by Kennelly and Affel.† Unfortunately in both papers the conductor thicknesses chosen were such that the effective depth of penetration was greater than the half thickness of the conductor so that it is not to be expected that good agreement will be obtained with the theoretical results for high frequencies.

Kennelly, Laws and Pierce made measurements over a range of frequencies from 250 to 5000 on copper strip conductors of thickness 0·159 cm. and ratios $b/a$ of 8, 16, 24. Over the range from 1000 to 5000 cycles a relation of the form (15) was found with values of $f(a/b)$ given in Table II, the theoretical high frequency values being added. It will be seen that the experimental values are a little over half the theoretical.

Table II.

| $b/a$. | 8. | 16. | 24. |
|---|---|---|---|
| $f(a/b)$ ........................................ | 0·73 | 0·62 | 0·51 |
| $f(a/b)$ theoretical .................... | 1·26 | 1·18 | 0·96 |

The work of Kennelly and Affel was carried out at frequencies up to $10^5$ cycles, but unfortunately the conductor thicknesses were chosen to be 0·0160 cm. and 0·0076 cm. so that again little agreement might be expected. For the 0·0160 cm. strip the values of $f(a/b)$ are again about half the infinite frequency values whilst the 0·0076 cm. strip has values for $f(a/b)$ practically equal to the infinite frequency value. The agreement, however, can only be considered to be accidental since a decisive experiment was performed showing that true skin effect was not present. The skin effect resistance ratio was measured for a strip 2·2 cm. wide and 0·0076 cm. thick and found to be 1·38 at $10^5$ cycles. It was then rolled into the form of a tube and the ratio found to diminish to 1·005. This shows that the increase of resistance observed for the flat strip is due not to non-uniformity of current in the thickness of the strip but to the crowding of the current to the edges of the strip.

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* 'Trans. Am. Inst. Elec. Eng.,' vol. 34, p. 1973 (1918).

† 'Proc. Inst. Radio Eng.,' vol. 4, p. 525 (1916).

The results for the proximity effect are equally useless for comparison with theory. One striking result of Kennelly and Affel shows, however, that an actual decrease is possible on bringing two conductors together. The resistance ratio was measured for the flat strips of section 2·54 × 0·0076 cm. and found to be 1·43 when isolated, diminishing to 1·00 when separated only by a distance of 0·0033 cm. This large decrease is, of course, due to the proximity effect making the current density uniform over the inside faces.

It is hoped that more satisfactory experimental results will shortly be available to test the theoretical work given.

I have in conclusion to express my indebtedness to Mr. E. B. Moullin, who first suggested the application of the electrostatic analysis to this problem, and to Dr. H. Lamb for his interest in the work.

# *Relative Velocities of the Alpha-Particles emitted by certain Radioactive Elements.*

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(Communicated by Sir Ernest Rutherford, P.R.S.—Received November 14, 1928.)

## I. *Introduction.*

The ordinary method of determining the velocity of alpha-particles depends on the measurement of the deflection of a beam of the rays in a magnetic field of known strength. The difficult measurement of the strength of the magnetic field gives rise to the largest source of error in the method. This source of error can be avoided in a direct comparison of the velocity of the alpha-particles with the velocity of the particles emitted by radium C′, which has been measured accurately by Rutherford and Robinson,[*] and by Briggs,[†] with excellent agreement. The method depends on the use of a combined source, consisting of the two radioactive elements to be compared. The radius of curvature of the path of the alpha-particles from each of the elements is measured in the usual way. Then the ratio of the velocities of the alpha-particles is equal to the ratio of the radii of curvature of their paths (after applying a small correction for the increase in mass at high velocities). In this manner the velocities of the rays from radium C′, thorium C and C′, and radium F, have been compared. Using Briggs' value of the velocity of the particles emitted by radium C′, the velocities of the others are calculated from the ratios thus obtained.

## II. *Apparatus.*

The apparatus is similar to that used by Briggs[‡] and described in his paper. Briefly, it consists of a rigid frame, supporting the wire source at one end, a partition with three slits in it parallel to the wire source in the centre, and a photographic plate at the other end. The distances from source to slits and from slits to plate were both about 10 cm., but varied somewhat with different measurements. This frame fits in a brass box between the poles of an electric magnet. The box was closed by a ground glass plate, which, when greased, permitted evacuation to $10^{-4}$ mm. A windlass raised a shutter which covered the slits while the chamber was being pumped out. The magnet and box were the ones used by Briggs.

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[*] 'Phil. Mag.,' vol. 28, p. 522 (1914).

[†] 'Roy. Soc. Proc.,' A, vol. 118, p. 549 (1928).

[‡] 'Roy. Soc. Proc.,' A, vol. 114, p. 341 (1927).

The magnetic field was excited by a 60-volt, 200 ampere-hour storage battery. A set of rheostats and a sensitive potentiometer-galvanometer circuit permitted the field current (6 amperes) to be kept constant (except for a slight drift discussed in Section V) to one part in 10,000 during periods up to 9 hours.

The sources were prepared on platinum wire of diameter 0·125 mm. and effective length 14 mm. Thorium active deposit was obtained on these wires by the usual method of exposing them, negatively charged, over radiothorium. Radium B and C were then distilled on the wires in a current of hydrogen from a piece of platinum foil previously exposed to radium emanation.

The polonium source was prepared by electrolysis and the thorium active deposit added by exposure to the emanation.

The radium C′ sources were equivalent in alpha ray activity to 10 to 20 mg. of radium, the combined thorium sources to 0·5 to 2·5 mg., and the polonium to 2 mg.

## III. *Measurements using Radium C′ and Thorium C Sources.*

The usual procedure was to expose the plates first for about 20 minutes, with the magnetic field current turned off, to obtain the lines produced by the undeflected beam of alpha-particles. The field was then put on and maintained constant for about 6 to 9 hours, to obtain the deflected lines.

The deflection of the beam of alpha-rays was measured by a microphotometer. Accuracy was limited by the grain structure of the plates and irregular and unsteady behaviour of the electrometer and photoelectric cells of the photometer. The effect of both sources of error is decreased by increasing the intensity of the lines. It was difficult to get sources on the fine wire used, of sufficient strength to give satisfactory line density, and although about 10 sources were obtained, the final result is based on only 4 of these. The rest were discarded because the contrast between the lines and the background irregularities did not permit sufficient accuracy. The strongest of the discarded plates gave results agreeing with the final value to one part in one thousand.

The photometer was of the kind designed to compare the density of the plate with an adjustable wedge. The intensity of the light transmitted was measured by a photoelectric cell and Lindemann electrometer. A second cell in the circuit compensated for variations in the intensity of the light source.

The compensation is not perfect, however, because the relation between light intensity and current is not perfectly linear, and the areas of the photoelectric cell, where the light from the wedge and from the plate strike it, differ somewhat in properties. As a result, the variation in the Pointolite lamp source usually makes a slight change in the measured density of a point on the plate during the time taken to measure a line. A number of points on the photometer curve were always checked before removing the plate from the instrument and if a change sufficient to cause appreciable error was found, the line was remeasured. A line on one of the plates had to be measured four times before the check was satisfactory.

The photometer curve of one of the plates is shown in fig. 1. The sloping sides of the peaks are almost straight over the central two-thirds of their height. A slight convexity (too slight to show in fig. 1) is straightened by a process which is equivalent to raising the intensity to a power slightly greater than one. The position of the line is taken as the abscissa of the intersection of the straight line sides of the peak produced upwards. The ratio of the velocities of two beams is equal to the ratio of their radii of curvature. The latter are obtained from the expression, which may readily be derived,*

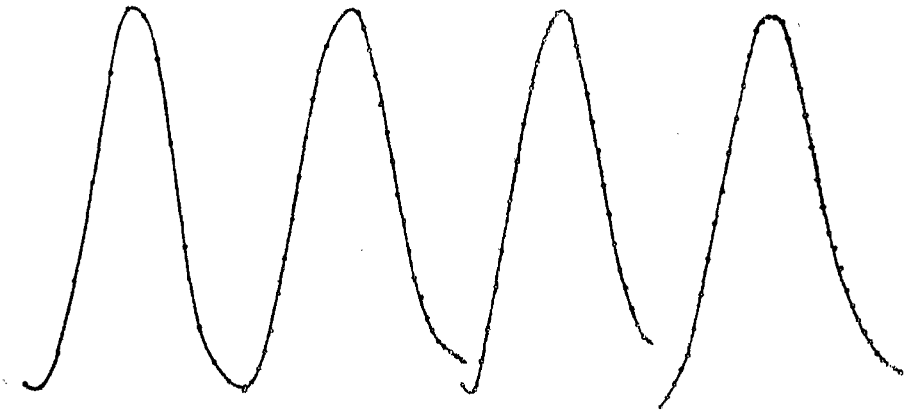

FIG. 1.

$$\rho = (l_2^2 + d^2)^{\frac{1}{2}} \, [(l_1 + l_2)^2 + d^2]^{\frac{1}{2}}/2d,$$

where $d$ is the distance between the deflected and undeflected lines, $l_1$ is the distance from source to slit, $l_2$ from slit to photographic plate. A small relativity correction for the mass of the moving alpha-particle must be applied to the ratios. A further correction for the variation in the magnet field strength (see Section V) is applied.

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* *Cf.* Briggs, 'Roy. Soc. Proc.,' A, vol. 114, p. 341 (1927).

Two of the plates are shown in fig. 2, *a* and *b*.

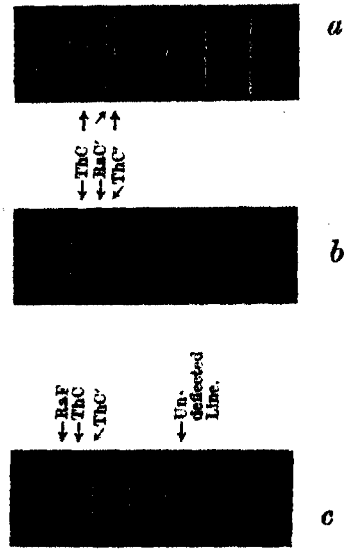

FIG. 2.

## IV. *Measurements using Radium F and Thorium C Sources.*

Two photographs were obtained with combined radium F and thorium C sources. The deflected lines were exposed first for about 5 hours and the undeflected ones for an hour and a half. The lines were found to be hazy on the low velocity side. This appeared to be due to impurities deposited on the wire with the polonium during electrolysis. The thorium deposit apparently penetrated the impurities to some extent. Briggs had a similar experience with electrolytic thorium sources. The high velocity sides of the peaks, however, were very sharp, and, when corrected for widening due to the obliquity of the beam to the photographic plate, had very closely the same slope as the undeflected lines. In this case the position of the line was taken to be the abscissa of the intersection of the straight line slope produced down to meet the background intensity. The alpha-particles coming to this edge of the undeflected line do not hit the plate perpendicularly, so the corresponding correction, amounting to 0·01 per cent. was calculated and applied to the results. One of the plates is reproduced in fig. 2*c*.

### V. *The Magnetic Field.*

Although, as already mentioned, the current through the magnet was kept quite constant, the actual magnetic field strength varied by a few tenths of a per cent. during a run. Thermal changes in permeability,[*] fatigue effects,[†] and hysteresis creepage caused by the small fluctuations in the exciting current probably account for this variation. The effect was measured by comparing the magnet field with the field of an air core solenoid by a null deflection method. Two search coils, one in the magnet field and the other in the solenoid field, were fastened rigidly to a single shaft so that they might be turned over together by rotating the shaft. They were connected in series to a sensitive galvanometer. The current through the solenoid was adjusted until the galvanometer was not deflected by rotating the search coils. Since the field of the air core solenoid was proportional to the current flowing through it, the percentage variation in the magnet field was equal to the percentage variation in the solenoid current required to restore the balance of the search coil circuit. The need of a second battery, controls and observer was avoided by connecting the solenoid, shunted to an adjustable resistance, in series with the magnet. The current through the solenoid was varied by adjusting the shunt resistance and the change measured by a milliammeter in series with the shunt. (Since the total current through the solenoid and shunt was kept constant, the increase in the current through one was equal to the decrease in the current through the other.) With this arrangement variations could be measured to 0·003 per cent. of the total field strength.

The variation in the magnet field strength, under the conditions of the velocity measurements, is plotted against time in fig. 3. As the rates of decay

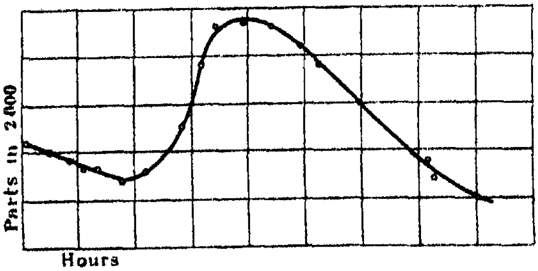

FIG. 3.

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[*] Curie, 'Ann. Chem. Phys.,' vol. 5, p. 289 (1895), and others.

[†] See for example Bozorth, 'Phys. Rev.,' vol. 32, p. 124 (1928).

of the radioactive elements were quite different, the mean field intensity during the exposure of the lines was not quite the same for all of them. The corresponding corrections were calculated for each plate from curve 3 and applied. It was found that the length of the central upward sloping part of the curve depended on the previous history of the magnetic field, but its slope and the shape of the rest of the curve were practically unaffected. Under the conditions of the actual velocity measurements, the length of this part of the curve varied by about 15 per cent. For this reason the size of the corrections is inaccurate to 0·02 per cent. of the final results.

The magnet exciting current was measured by finding the drop in potential across a 0·1 ohm standard resistance connected in series. The resistance of this increased about 0·05 per cent. due to heating during the measurement. This change was measured by a simple Wheatstone Bridge. The resistance was plotted against time, and the necessary corrections found from this curve were applied to curve 3.

The residual field of the magnet averaged ± 10 gauss. This results in a probable error of 0·015 per cent. in the radium F–thorium C′ ratio and smaller errors in the other ratios. This source of error might have been avoided by measuring the residual field each time, but unfortunately its size was underestimated until it was actually measured after the work was completed.

## VI. *Other Sources of Error.*

Error may result from shrinkage or expansion of the gelatin on the photographic plates. This was investigated by exposing a photographic plate under a stencil. When the stencil was replaced over the developed image, no difference between the size of the stencil and the image was found on either dry or humid days, although a difference in length of 0·005 per cent. could easily have been detected.

Inaccuracy of the photometer screw introduces quite negligible error in the method, provided the pitch of the screw is uniform throughout its length. This was tested by using different parts of the screw in measuring the distance between two scratches on a blackened microscope slide. These measurements agreed to within 0·01 per cent.

Considerable error may arise from a slight tilt of the photographic plate with respect to the plane perpendicular to the undeflected beam of alpha-particles. The slope of the plate holder was adjusted by sensitive method depending on the reflection of a normally incident beam of light, so that the errors due to such a tilt are less than 0·01 per cent.

The errors in measuring $l_1$ and $l_2$, (Section III), produce a negligible error in the result.

## VIII. *Results.*

The results, fully corrected for variation in the field strength and relativity mass, are given in Table I. The weighted means are probably correct to 0·05 per cent. The weights are assigned on consideration of the degree of contrast of the plates. The velocities were found to be in the proportions:—

Table I.—Ratios of Velocities of Alpha-Particles.

| Plate. | ThC′/RaC′. | Weight. | ThC′/ThC. | Weight. | ThC′/RaF. | Weight. |
|---|---|---|---|---|---|---|
| 12 | 1·0681 | 1 | 1·2018 | 1 | | |
| 6 | | | 1·2014 | 1 | | |
| 13 | 1·0677 | 1 | | | | |
| 5 | 1·0680 | 1 | 1·2015 | ½ | | |
| 14 | | | 1·2015 | ½ | 1·2890 | ½ |
| 15 | | | 1·2024 | ½ | 1·2904 | ½ |
| Weighted mean | 1·0679 ± 0·0003 | | 1·2017 ± 0·0003. | | 1·2902 ± 0·0006 | |

Radium F : Thorium C′ = 0·8277 : 1·0679

Thorium C : Radium C′ : Thorium C′ = 0·8885 : 1·0000 : 1·0679

Using Briggs' value of the velocity of RaC′ alpha-particles $1 \cdot 923 \times 10^9$ cm./sec., the others are calculated to be:—

| | |
|---|---|
| Thorium C ................ | $1 \cdot 709 \times 10^9$ cm./sec. |
| Thorium C′ ................ | $2 \cdot 054 \times 10^9$ cm./sec. |
| Radium F ................ | $1 \cdot 592 \times 10^9$ cm./sec. |

The probable error in the velocity of the alpha-particles from RaF is 0·15 per cent., and from ThC and ThC′ is 0·1 per cent.

By direct measurement, Mlle. Curie has found the velocity of RaF alpha-particles to be $1 \cdot 593 \times 10^9$ cm./sec., a value in good agreement with that obtained above.

The Kinetic energies are in the proportion:—

Radium F : Thorium C′ = 0·6842 : 1·1407

Thorium C : Radium C′ : Thorium C′ = 0·7888 : 1·0000 : 1·1407,

with a probable error of 0·1 per cent.

In Table II the above velocities are tabulated with those obtained by Briggs, and those calculated from the ranges by the Geiger formula, $V = \sqrt[3]{aR}$.

Briggs' measured velocity of RaC′ alpha-particles, $1\cdot923 \times 10^9$ cm./sec., is taken as the standard for these calculations, and the ranges used are the extrapolated ranges* found by Henderson for RaC′ and ThC, and by Geiger for RaF. The difference between the calculated ranges and the ranges obtained from these measurements is considerably greater than the probable experimental errors. In fig. 4 the excess of the experimental range over the calculated is plotted against the range. The curve gives the correction to be added to the expression $(a\mathrm{R})^{\frac{1}{3}}$ when calculating the velocity of alpha-particles from their extrapolated range R, where $a$ has the value $1\cdot0228 \times 10^{-27}$ cm.$^2$/sec$^3$.

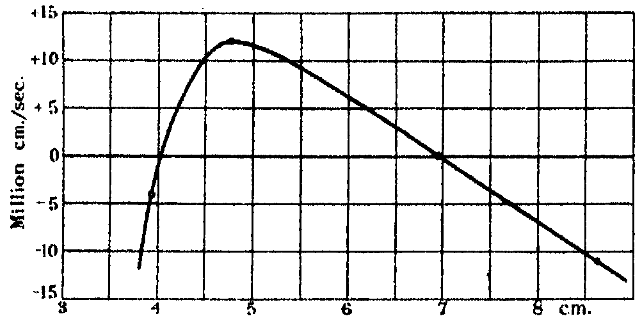

FIG. 4.

Although the extrapolated range has perhaps less theoretical significance than the various kinds of "mean range" obtained by other methods, and differs considerably from them, it has been used in the above calculations because it has been measured in almost the same way for most of the alpha-particles emitted by the radioactive elements. It is possible to calculate corrections to be applied to this range to obtain the others, but it is found that the probable error in the corrections is very large and probably considerably greater than the errors in the measurements. Even the other ranges are not the R of theory, so that it is best for purposes of interpolation to use consistently the kind of range which has been measured accurately for the greatest number of substances.

The author desires to thank Sir Ernest Rutherford for his encouraging interest in this work. He is very gratefully indebted to Mr. J. P. Gott for his invaluable assistance in the magnetic field measurements.

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* The expression "extrapolated range" is used for brevity to mean the range obtained, by these and other authors, by producing the nearly straight oblique part of an ionisation curve, downwards to intersect the range axis, and taking the abscissa of the intersection (measured, of course, from that representing the position of the source).

Table II.

| Substance. | Range. | Velocity from $\sqrt[3]{aR}$. | Measured velocity. | Velocity from Briggs' ratios. | Velocity from these measurements. |
|---|---|---|---|---|---|
| | | $\times 10^9$ cm./sec. | $\times 10^9$ cm./sec. | $\times 10^9$ cm./sec. | $\times 10^9$ cm./sec. |
| RaC′ | 6·953 (Henderson) | — | 1·923 (Briggs) | — | — |
| ThC | 4·778 (Henderson) | 1·697 | | 1·705 | 1·709 |
| ThC′ | 8·616 (Henderson) | 2·065 | | 2·053 | 2·054 |
| RaF | 3·87 (Curie)<br>3·925 (Geiger) | 1·582<br>1·588 | 1·593 (Curie) | | 1·592 |

## *Summary.*

The ratio of the velocities of the alpha-particles from RaC′, ThC, ThC′ and RaF was measured by the magnetic field method and was found to be

$$\text{RaF} : \text{ThC} : \text{RaC}' : \text{ThC}' = 0{\cdot}8277 : 0{\cdot}8885 : 1{\cdot}0000 : 1{\cdot}0679,$$

with a probable error of 0·05 per cent. Using Briggs' value of the velocity of RaC′, $1{\cdot}923 \times 10^9$ cm./sec., the velocities are calculated to be :—

| | |
|---|---|
| Thorium C ................ | $1{\cdot}709 \times 10^9$ cm./sec. |
| Thorium C′ ................ | $2{\cdot}054 \times 10^9$ cm./sec. |
| Radium F ................ | $1{\cdot}592 \times 10^9$ cm./sec. |

# *The Products of Partial Hydrogenation of Higher Monoethylenic Esters.*

By T. P. Hilditch, D.Sc., and N. L. Vidyarthi, Liverpool University.

(Communicated by E. F. Armstrong, F.R.S.—Received November 14, 1928.)

The formation of "iso-oleic" acids during hydrogenation of oleic ($\Delta^{9:10}$-octadecenoic) acid or its esters is of importance in connection with the general theory of catalytic action at solid surfaces.* The constitution of these isomeric acids has therefore been re-examined by means of the oxidising action of potassium permanganate upon hot acetone solutions of their unsaturated esters, a method which has been shown to break such compounds up almost quantitatively into derivatives of the corresponding monobasic and dibasic acids† :—

$$CH_3 . [CH_2]x . CH : CH . [CH_2]y . COOR \rightarrow CH_3 . [CH_2]x . COOH + COOH . [CH_2]y . COOR.$$

Moore‡ has already shown that during hydrogenation a state of equilibrium is reached between the amounts of ordinary oleic acid present and the isomeric forms, and that the latter include elaidic acid together with one or more iso-oleic acids produced by migration of the ethylenic linkage ($\Delta^{11:12}$-octadecenoic acid being suggested as a possible product).

Our present results indicate that *cis*- and *trans*-modifications of each isomeric oleic acid are formed, and that the iso-oleic acids in which migration of the ethylenic linkage has occurred have the latter in either of the two positions adjacent to the original: thus, from $\Delta^{9:10}$-octadecenoic acid are obtained both $\Delta^{8:9}$-and $\Delta^{10:11}$-octadecenoic acids. This state of affairs holds in the case of the partially-hydrogenated methyl ester of ordinary oleic acid, and also in those of palmitoleic ($\Delta^{9:10}$-hexadecenoic) acid from whale oil, and erucic ($\Delta^{13:14}$-docosenoic) acid from rape or mustard seed oils.

Following Moore's observation that equilibrium between the various isomeric oleic acids is reached after about one-third of the ethylenic compounds have been converted into the saturated derivatives, methyl oleate, methyl palmitoleate and methyl erucate were treated with hydrogen in presence of nickel mounted on kieselguhr, at temperatures varying from 114° to 220°, until their iodine values were reduced by about 30 per cent.

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* *Cf.* Armstrong and Hilditch, 'Roy. Soc. Proc.,' A, vol. 96, p. 325 (1919).

† Armstrong and Hilditch, 'J. Soc. Chem. Ind.,' vol. 44, p. 43 T (1925).

‡ 'J. Soc. Chem. Ind.,' vol. 38, p. 320 T (1919).

An attempt was made to effect a separation of the iso-oleic acids by fractional precipitation as lead salts from solution in alcohol.* The lead salts of the isomeric solid oleic acids were, however, closely similar in solubility, so that little or no separation resulted. This procedure nevertheless permitted us to obtain a specimen of the "liquid oleic acids" free from solid iso-oleic acids, and oxidation of the methyl esters from this fraction showed that, in addition to ordinary $\Delta^{9:10}$-oleic acid, subsidiary quantities of $\Delta^{8:9}$- and $\Delta^{10:11}$-octadecenoic acids were present in the form of acids which furnished soluble lead salts (*cf.* p. 560).

The conclusions now put forward are based mainly upon the results of direct oxidation of the partially-hydrogenated esters, followed by resolution of the resulting mixture of monocarboxylic and dicarboxylic acids. The latter has been carried out in more detail than formerly: the mixture of monocarboxylic and dicarboxylic acids was first heated under diminished pressure until practically all the former had distilled over, after which the residue was converted into acidic chlorides by means of thionyl chloride and then heated with methyl alcohol, the dimethyl esters of these acids being subsequently obtained free from acidic products and fractionated in a vacuum. The distillate of monocarboxylic acids was converted into methyl esters in presence of 2 to 3 per cent. of sulphuric acid and the latter were purified and also fractionally distilled.

We rely mainly upon the evidence afforded by the dicarboxylic acids, the identity of which has been satisfactorily established; to some extent, also, the separation of these is of a quantitative character, and a rough indication can be given of the probable proportions of the isomeric acids present. The fractional distillation is, however, not so easy as in the case of methyl esters of the higher natural fatty acids, and the equivalents of the products are too close to permit of any accurate calculation being made. The monocarboxylic acids are still less suited to quantitative treatment; their examination has led, nevertheless, to the qualitative identification of components present, and serves to confirm conclusions drawn from the dicarboxylic acids.

Since the results show consistently that, commencing for example with $\Delta^{9:10}$-oleic acid, a mixture of $\Delta^{8:9}$-, $\Delta^{9:10}$- and $\Delta^{10:11}$-octadecenoic acids is obtained, it is necessary to be assured that the $\Delta^{8:9}$- and $\Delta^{10:11}$-acid products have not been formed as a result of secondary oxidation of $\Delta^{9:10}$- and (possible) $\Delta^{11:12}$-acids, more especially as it is known that dicarboxylic acids of the even-number series are more stable than the adjacent members of the odd-number series.[*] That permanganate-acetone oxidation of methyl oleate and similar esters is not accompanied by any secondary oxidation of the primary acidic products is proved by the facts that oxidation of methyl oleate, methyl palmitoleate and methyl erucate yields in each case only one monocarboxylic and one dicarboxylic acid, and that the products all belong to the odd-number series. As will be seen later, identification of the even-number dicarboxylic acids is very easy owing to their relative insolubility in chloroform and, whilst we have invariably observed their presence readily in the oxidation of partially-hydrogenated esters, we have never detected them when the esters of the natural, non-hydrogenated acids have been similarly oxidised. Moreover, the monocarboxylic acids have always been found to correspond with the dicarboxylic acid scission products ; for example, from partially hydrogenated $\Delta^{9:10}$-oleic acid we have obtained suberic, azelaic and sebacic acids (but no undecane-dicarboxylic acid)[†] together with decoic, nonoic and octoic acids.

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* *Cf.* Twitchell, 'J. Ind. Eng. Chem.,' vol. 13, p. 806 (1921).

The data obtained may be summarised conveniently in tabular form, showing (i) the scission-products which have been identified, and (ii), from the dicarboxylic esters, a very rough indication of the probable equivalent proportions of the various isomeric acids present.

It is clear that in all cases ethylenic linkages appear in adjacent positions to that occupied by the original centre of unsaturation. The proportion of iso-oleic acids formed appears to vary with the length of the carbon chain, in addition to the already recognised variation with the temperature of hydrogenation.

It was emphasised by E. F. Armstrong and one of the present authors[‡] that the production of " iso-oleic acids of hydrogenation " was important evidence of the association of the organic compound undergoing change with the metal catalyst at the surface of the latter ; and it was suggested that, whilst formation of geometrical isomerides might proceed, without actual hydrogenation, during adsorption and desorption of an ethylenic compound at the catalyst surface, the production of iso-oleic acids in which migration of the double bond had taken place was probably due to dehydrogenation of the freshly-formed saturated ester at a preferred position in the carbon chain.

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[*] *Cf.* Challenor and Thorpe, ' J. Chem. Soc.,' vol. 123, p. 2480 (1923).

[†] We have named the higher dicarboxylic acids according to the total number of carbon atoms present ; *e.g.* $COOH . [CH_2]_9 . COOH$ has been called undecane-dicarboxylic acid.

[‡] *Loc. cit.*

| **Ester partially hydrogenated.** | Temperature. | Oleic acids observed. | Approximate proportions. | Dicarboxylic acids identified. | Monocarboxylic acids present. |
|---|---|---|---|---|---|
| **Methyl oleate** ($\Delta^{9:10}$-octadecenoate)* | 217–220° | $\Delta^{8:9}$-octadecenoic | 7 | Suberic ................ | Decoic. |
| | | $\Delta^{9:10}$ ,, | 10 | Azelaic ................ | Nonoic. |
| | | $\Delta^{10:11}$ ,, | 7 | Sebacic ................ | Octoic. |
| | | $\Delta^{12:13}$ ,, | 1 | Dodecane dicarboxylic | Hexoic. |
| | 114–118 | $\Delta^{8:9}$-octadecenoic | 7 | Suberic ................ | Decoic. |
| | | $\Delta^{9:10}$ ,, | 10 | Azelaic ................ | Nonoic. |
| | | $\Delta^{10:11}$ ,, | 3 | Sebacic ................ | Octoic. |
| | | $\Delta^{12:13}$ ,, | 1 | Dodecane dicarboxylic | Hexoic. |
| **Methyl palmitoleate** ($\Delta^{9:10}$-hexadecenoate) | 170–180 | $\Delta^{8:9}$-hexadecenoic | 5 | Suberic ................ | Octoic. |
| | | $\Delta^{9:10}$ ,, | 10 | Azelaic ................ | Heptoic. |
| | | $\Delta^{10:11}$ ,, | 5 | Sebacic ................ | Hexoic. |
| **Methyl erucate** ($\Delta^{13:14}$-docosenoate) | 200 | $\Delta^{12:13}$-docosenoic | — | Dodecane dicarboxylic | Not examined. |
| | | $\Delta^{13:14}$ ,, | — | Tridecane dicarboxylic (brassylic) | |
| | | ($\Delta^{14:15}$ ,, ) | — | ? Tetradecane dicarboxylic | |

* This ester contained a small proportion (about 3·5 per cent.) of methyl linoleate.

The small amount of $\Delta^{12:13}$-octadecenoic acid observed in each of the products from methyl oleate is considered almost certainly to have been produced by concurrent hydrogenation of methyl linoleate, which was present in small quantity in the original ester employed (*cf.* the following communication, p. 567).

In the case of partially hydrogenated methyl erucate, the highest dicarboxylic ester was left almost entirely in the distillation residue, and in consequence was not satisfactorily characterised; the data in this instance were not adapted to a quantitative estimate (*cf.* p. 562).

The data now put forward enable this explanation to be re-stated in a more simple form. If, in the association of an ethylenic linkage with nickel

$$\begin{array}{c}-CH_2-CH_2-\underset{\vdots}{C}H=\underset{\vdots}{C}H-CH_2-CH_2-\\ -Ni-Ni-\end{array}$$

followed by union with hydrogen and formation of the corresponding saturated compound, the possibility of reversal of the process (dehydrogenation) before the saturated compound leaves the catalyst surface is considered, it appears most likely that such dehydrogenation will occur in the same position as that occupied by the original double bond, and lead to the formation of the original ethylenic compound or its geometrically isomeric form. Alternatively, dehydrogenation may ensue on either side of either of the carbon atoms which, as components of the original ethylenic linkage, were brought into association with the catalyst.

We are thus led to ascribe the formation of both geometrical and structural isomeric forms of oleic acids during hydrogenation to the operation of reversed hydrogenation (dehydrogenation) prior to the dis-association (or " desorption ") of the freshly-formed saturated compound from the catalyst surface. This point of view also conforms with Moore's observation* that no isomeric oleic acids are produced unless hydrogenation is actually proceeding.

It would seem likely that the presence of a somewhat lengthy, unsubstituted, skeleton of carbon atoms is necessary before isomerisation of this kind is developed to any extent, since it has so far only been met with in the case of the higher unsaturated fatty acids and esters. In the hydrogenation of unsaturated cyclic compounds, terpenes and other derivatives, it most frequently happens that unsubstituted chains of carbon atoms are not contiguous to the unsaturated centres; (the presence of substituents, even the simplest alkyl groups, is known to exercise considerable influence on the course of hydrogenation).† On the other hand, the production of a mixture of geometrical isomerides during hydrogenation is a frequent phenomenon, for example, in the case of substituted phenols, such as thymol or the cresols.

### *Preparation of the Partially-hydrogenated Esters.*

*Methyl Oleate.*—The oleic acid was derived from olive oil and had been purified from saturated acids and linoleic acid in the usual manner. The methyl oleate from the purified acid was distilled under reduced pressure (iodine absorption 89·0 per cent., corresponding to a content of 3·5 per cent. of methyl linoleate).

*Methyl Palmitoleate.*—This was prepared from pure palmitoleic acid isolated from whale oil‡ and had an iodine absorption of 93·0 per cent.

*Methyl Erucate.*—This was obtained by redistillation of fractions of the almost pure ester obtained in the course of analyses of rape and mustard seed oils;§ it contained small amounts of methyl oleate and of higher saturated methyl esters and possessed an iodine absorption of 71·3 per cent.

Each ester was hydrogenated at the desired temperature in presence of nickel mounted on kieselguhr (15 per cent. Ni); the concentration of metallic nickel present with the ester was about 0·5 per cent. The following figures show the extent of hydrogenation in each case studied :—

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* *Loc. cit.*, p. 323 T.

† Lebedev, Kobliansky and Yakubchik, 'J. Chem. Soc.,' vol. 127, p. 417 (1925).

‡ Armstrong and Hilditch, 'J. Soc. Chem. Ind.,' vol. 44, p. 181 T (1925).

§ Hilditch, Riley and Vidyarthi, 'J. Soc. Chem. Ind.,' vol. 46, p. 462 T (1927).

| Ester. | Temperature. | Hydrogenated ester. Iodine absn. per cent. |
|---|---|---|
| | ° | |
| Methyl oleate (125 g.) | 217–220 | 54·4 |
| ,, (150 g.) | 200 | 56·2 |
| ,, (110 g.) | 114–118 | 59·4 |
| Methyl palmitoleate (100 g.) | 170–180 | 60·2 |
| Methyl erucate (107 g.) | 200 | 45·3 |

### *Oxidation of the Partially-hydrogenated Esters.*

The ester (1 part) was dissolved in acetone (10 parts) and to the solution powdered potassium permanganate (3 parts) was gradually added, the mixture being thoroughly shaken after each addition and maintained in a state of gentle ebullition under a reflux condenser; subsequently, it was refluxed for a short time and the acetone removed by distillation. The residual solid cake was mixed with sodium bisulphite and dissolved in hot water, when dilute sulphuric acid was added until all the manganese compounds present had been reduced to the manganous condition. The cooled decolorised solution was extracted with ether, and the ethereal extract washed with dilute sodium carbonate solution to remove the acidic oxidation products. The neutral esters recovered from the ether still contained, as a rule, some unattacked oleic esters, and were therefore submitted to a repetition of the oxidation process. There was eventually obtained (*a*) neutral saturated material of negligible iodine absorption, and (*b*) a mixture of acidic products of oxidation (free monocarboxylic acids and monomethyl esters of dicarboxylic acids).

The acidic products were boiled for some time with aqueous caustic soda and the mixture of free mono- and di-carboxylic acids recovered and distilled from a plain Willstätter flask under low pressure. Practically all the monocarboxylic acids distilled over, accompanied by only small proportions of the most volatile dicarboxylic acids present, whilst only minor amounts of the least volatile monocarboxylic acid remained in the residue. This procedure gave a more complete separation than fractional distillation of the mixed mono- and di-carboxylic esters, or their separation by the use of a solvent such as petroleum ether.

Each group of acids was converted into neutral methyl esters and fractionally distilled under reduced pressure.

The various fractions of esters obtained were hydrolysed and the free acids examined. Attempts to separate the homologous dicarboxylic acids by selective crystallisation or precipitation in the form of magnesium or other salts were unsuccessful, but it was found comparatively easy to separate an acid containing an odd number of carbon atoms from one containing an even number of carbon atoms by taking advantage of the relatively sparing solubility of the latter in chloroform.

### *Methyl Oleate* (*Hydrogenated at* 217–220°).

The partially-hydrogenated ester (115 g.) yielded on oxidation (*a*) neutral material (39·4 g., iodine absorption 0·1 per cent.—methyl stearate produced during hydrogenation), and (*b*) acidic products which were resolved as described into monocarboxylic acids (34 g.) and dicarboxylic acids (41 g.).

Dicarboxylic Esters.

| No. | *g.* | B.p./0·5 mm. | Equivalent. | Dicarboxylic acids identified. |
|---|---|---|---|---|
| | | ° | | |
| 1 | 3·1 | 62–89 | 103·0 | Suberic 139–140° (139–140°*) (equivalent, found, 86·8; calc. 87·0). |
| 2 | 7·7 | 89–91 | 104·5 | Suberic 139–140° (139–140°); azelaic 102–103° (103–104°). |
| 3 | 3·1 | 92–93 | 108·0 | |
| 4 | 2·2 | 94–98 | 111·5 | Azelaic acid, 105°; sebacic acid 129–130°. |
| 5 | 1·8 | 98–105 | 114·4 | Sebacic acid, 130°. |
| 6 | 1·9 | 105–113 | 117·3 | Sebacic acid, 131°, and an acid, m.p. 106–107° (indef.)†, which was apparently a mixture of sebacic and dodecane dicarboxylic acids (equivalent, found, 113·2). |
| 7 | 4·5 | Residue | 135·0 | |
| | 24·3 | | | |

* Melting-points in brackets are those of mixtures with authentic specimens.

† Mixed melting-point tests indicated that this acid was neither azelaic nor undecane dicarboxylic acid.

The last fraction and the residue contained small quantities of a dicarboxylic acid of higher molecular weight than sebacic acid—probably dodecane dicarboxylic acid, $C_{12}H_{22}O_4$, from the oxidation of $\Delta^{12:13}$-octadecenoic acid emanating from the small amount of methyl linoleate originally present.

Monocarboxylic Esters.

| No. | *g.* | B.p./15 mm. | Equivalent. |
|---|---|---|---|
| | | ° | |
| 1 | 1·9 | 65–80 | 143 |
| 2 | 1·8 | 80–87 | 148 |
| 3 | 2·2 | 87–93 | 148 |
| 4 | 2·1 | 93–96 | 154 |
| 5 | 3·1 | 97–103 | 161 |
| 6 | 8·6 | 103–115 | 161 |
| 7 | 4·2 | Residue | 150 |
| | 23·9 | | |

The lower fractions contained an ester, of lower molecular weight than methyl caprylate, which appeared to be methyl caproate from oxidation of $\Delta^{12:13}$-octadecenoic acid (already mentioned as emanating from the small amount of methyl linoleate originally present).

Fractions 6 and 7 consisted mainly of methyl nonoate, admixed with methyl caprate and some methyl suberate; the free acids from the esters yielded a portion soluble in hot water which, after crystallisation from chloroform, melted at 134–136°; the water-insoluble portion was fractionally separated from alcohol in the form of lead salts, the least soluble of which yielded a solid acid which melted at 25–26° after crystallising from dilute alcohol (capric acid, m.p. 31°).

The lithium salts of the acids from fraction 4 were crystallised from 70 per cent. alcohol, and the acid liberated from the crystals obtained melted at 10–11° (caprylic acid, m.p. 13°).

*Occurrence of Isomeric Oleic Acids in the " Liquid " Oleic Acids of Hydrogenation.*

Some evidence that both geometrically isomeric forms of $\Delta^{8:9}$- and $\Delta^{10:11}$-octadecenoic acids were present was obtained by fractional precipitation of the hydrogenated acids in the form of lead salts. The fatty acids (140 g.) (from methyl oleate which had been hydrogenated at 200° C. until the iodine absorption was 56·2) were dissolved in 95 per cent. alcohol (700 c.c.) and to the boiling solution was added a hot solution of lead acetate (25 g.) in alcohol (700 c.c.). After standing overnight the deposited lead salts were filtered from the cold solution, and the latter was heated to boiling and mixed with a further solution of lead acetate (25 g.), alcohol being distilled off so that the bulk of the final mixture was maintained the same as in the first case. This procedure was repeated until no further deposit of crystalline lead salts was obtained. The acids recovered from the lead salt fractions were as follows :—

| No. | *g.* | Iod. absn. | |
|---|---|---|---|
| 1 | 39·8 | 20·8 | Mainly stearic acid. |
| 2 | 30·7 | 64·8 | Some stearic acid present. |
| 3 | 10·3 | 72·2 | |
| 4 | 17·0 | 73·7 | |
| 5 | 42·0 | 71·6 | Acids from soluble lead salts finally left in solution. |

Fractions 2 and 4 were reconverted into methyl esters and oxidised as described above, followed by examination of the dicarboxylic acids produced; it was found that azelaic acid, together with subsidiary amounts of suberic and sebacic acids, was present in each case. In other words, the "solid" iso-oleic acids thus separated were always mixtures, and no selective precipitation of one or other isomeride could be attained (*cf.* p. 553).

Fraction 5, comprising the acids which yielded freely soluble lead salts, was converted into methyl esters, the latter (35·3 g.) were subjected to the oxidation process, and the dimethyl esters of thé resulting dicarboxylic acids were fractionally distilled :—

| No. | *g.* | B.p./0·5 mm. | Equivalent. | Acids identified. |
|---|---|---|---|---|
| | | ° | | |
| 1 | 3·4 | 75–85 | 107·5 | Suberic, 137–138° (138–139°). |
| 2 | 4·1 | 85–99 | 106·4 | Suberic, 137–138° (138–139°) ; azelaic, 102–103°. |
| 3 | 3·1 | 101–103 | 111·6 | Azelaic, 102–103°. |
| 4 | 3·5 | Residue | 116·0 | Sebacic, 126–127° (129–130°). |
| | 14·1 | | | |

This result shows that the $\Delta^{8:9}$- and $\Delta^{10:11}$-octadecenoic acids are present in forms which give rise to comparatively soluble lead salts, *i.e.*, in *cis*- as well as *trans*-modifications.

### *Methyl Oleate* (*Hydrogenated at* 114–118°).

The partially-hydrogenated product (93 g.) was oxidised as above, and gave neutral (non-oxidised) products (29 g., iodine absorption 1·1 per cent., *i.e.*, methyl stearate), monocarboxylic acids (23 g.) and dicarboxylic acids (38 g.).

Dicarboxylic Esters.

| No. | *g.* | B.p./0·5 mm. | Equivalent. | Dicarboxylic acids identified. |
|---|---|---|---|---|
| | | ° | | |
| 1 | 6·3 | 60–85 | 115·5 | Suberic, 138–139° (138–139°) ; azelaic, 103–104° (103–104°). |
| 2 | 10·2 | 85–86 | 104·0 | Suberic, 139–140° (139–140°) ; azelaic, 102–103°. |
| 3 | 6·7 | 87–90 | 106·0 | Suberic (small quantity) ; azelaic, 102–103°. |
| 4 | 3·9 | 91–95 | 107·0 | |
| 5 | 2·3 | 95–105 | 112·0 | Sebacic, 129–130° (131–132°). |
| 6 | 7·1 | Residue | 118·0 | Sebacic, 127–128° (131–132°) ; dodecane dicarboxylic acid (?). |
| | 36·5 | | | |

Monocarboxylic Esters.

| No. | *g.* | B.p./10 mm. | Equivalent. |
|---|---|---|---|
| | | ° | |
| 1 | 2·5 | 45–55 | 143·0 |
| 2 | 5·2 | 55–62 | 157·0 |
| 3 | 5·5 | 62–65 | 162·4 |
| 4 | 5·2 | Residue | 187·6 |
| | 18·4 | | |

The individual fractions of the monocarboxylic esters were not closely examined.

*Methyl Palmitoleate* (*Hydrogenated at* 170–180°).

The hydrogenated ester (97 g.) was oxidised as in the previous cases, when there were obtained neutral (non-oxidised) esters (32·5 g., iodine absorption 0·7 per cent.—methyl palmitate), monocarboxylic acids (14·5 g.) and dicarboxylic acids (34·7 g.).

Dicarboxylic Esters.

| No. | *g.* | B.p./0·3 mm. | Equivalent. | Dicarboxylic acids identified. |
|---|---|---|---|---|
| | | ° | | |
| 1 | 2·7 | 70–85 | 106·8 | Suberic, 139–140° (139–140°); azelaic, 103–104° (103–104°). |
| 2 | 3·8 | 85–91 | 101·5 | Suberic, 139–140° (139–140°); azelaic, 103–104° (103–104°). |
| 3 | 7·9 | 91–95 | 107·2 | Suberic, 139–140° (139–140°); azelaic, 102–103° (104–105°). |
| 4 | 6·0 | 95–100 | 111·0 | |
| 5 | 2·9 | 100–106 | 112·0 | Azelaic, 104–105° (104–105°). |
| 6 | 6·2 | Residue | 126·9 | Sebacic, 129–130° (130–131°). |
| | 29·5 | | | |

Monocarboxylic Esters.

| No. | *g.* | B.p./760 mm. | Equivalent. |
|---|---|---|---|
| | | ° | |
| 1 | 1·7 | 140–150 | 130·1 |
| 2 | 2·0 | 150–160 | 139·0 |
| 3 | 2·7 | 160–165 | 143·0 |
| 4 | 5·9 | 165 | 151·8 |
| 5 | 0·8 | Residue | Not examined |
| | 13·1 | | |

The dicarboxylic acids identified were again suberic, azelaic and sebacic; whilst the complementary examination of the monocarboxylic esters gave a general indication of the presence of methyl heptoate (equivalent 144) in quantity, together with an ester of higher and of lower molecular weight, at the same time not disclosing the presence of any ester lower than methyl hexoate.

### *Methyl Erucate* (*Hydrogenated at* 200°).

The hydrogenated ester yielded on oxidation neutral (non-oxidised) products (32 g., iodine absorption 1·2 per cent.—methyl behenate), monocarboxylic acids (16 g.) and dicarboxylic acids (34 g.).

Dicarboxylic Esters.

| No. | *g.* | B.p./0·3 mm. | Equivalent. | Dicarboxylic acids identified. |
|---|---|---|---|---|
| 1 | 4·2 | 100–110 | 124·9 | Suberic, 138° (trace); dodecane dicarboxylic acid, 124–125°. |
| 2 | 5·9 | 112–120 | 121·9 | Dodecane dicarboxylic acid, 124–125°. |
| 3 | 8·3 | 121–127 | 130·0 | Dodecane dicarboxylic acid, 124–125° (equivalent found, 115·2; calc. 115). |
| 4 | 4·6 | 127–133 | 137·8 | Brassylic (tridecane dicarboxylic), 110–111° (111–112°). |
| 5 | 2·9 | 135–140 | 137·8 | Brassylic, equivalent found 123·0; calc. 122. |
| 6 | 7·6 | Residue | 150·3 | ? Tetradecane dicarboxylic acid.* |
| | 33·5 | | | |

* The residue contained an unusually large amount of decomposition products, including traces of saturated higher fatty acids; the latter were removed by solution in petrol ether, whilst neutral products were subsequently extracted with ether from a solution of the sodium salts; the recovered, purified acids had an equivalent of 125, corresponding with a mixture of tri- and tetradecane carboxylic acids, but we did not succeed in isolating any individual acid by crystallisation.

In view of the indefinite evidence as to the last-named acid, and also of the evident presence of the isomeric acids emanating from the small amount of oleate present in the original methyl erucate, we have not felt justified in attempting any approximate estimate of the proportion of the isomeric erucic acids of hydrogenation formed. From the qualitative evidence, however, it is clear that in addition to $\Delta^{13:14}$-docosenoic acid, the isomeric $\Delta^{12:13}$-acid was present in quantity, whilst another acid, almost certainly $\Delta^{14:15}$-docosenoic, had also been produced.

## Summary.

The isomeric forms of the higher monoethylenic fatty acids which are produced during hydrogenation have been proved, in the case of methyl oleate, methyl palmitoleate and methyl erucate, to consist of a mixture of acids in which the ethylenic linkage is adjacent to the position which it occupied in the original compound; these acids, together with the original position isomeride, are almost certainly present in both *cis*- and *trans*-forms in the hydrogenated products.

The bearing of these results upon the general theory of contact action at solid surfaces is considered, and it is shown that they are fully in harmony with the explanation put forward previously.*

We desire to thank the Government of Bihar and Orissa for assistance rendered to one of us (N.L.V.) during this investigation.

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# The Products of Partial Hydrogenation of some Higher Polyethylenic Esters.

By T. P. Hilditch, D.Sc., and N. L. Vidyarthi, Liverpool University.

(Communicated by E. F. Armstrong, F.R.S.—Received November 14, 1928.)

It is well known that, when an unsaturated higher fatty acid ester (such as methyl linoleate or linolenate) is hydrogenated, the process is largely selective,† and no fully-saturated ester is produced until nearly 90 per cent. of the polyethylenic ester has been transformed into monoethylenic compounds (*i.e.*, methyl oleate and iso-oleates). Accordingly, if the monoethylenic esters produced by selective hydrogenation of, for example, methyl linolenate.

$$CH_3 . CH_2 . CH : CH . CH_2 . CH : CH . CH_2 . CH : CH . [CH_2]_7 . COOMe$$

were a mixture of the esters of $\Delta^{9:10}$-, $\Delta^{12:13}$-, and $\Delta^{15:16}$-octadecenoic acids in more or less equivalent proportions, it should be possible to determine the position of the ethylenic linkages in the original compound by careful oxidation of the mixture of methyl oleates formed, according to the methods given in the preceding communication.*

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* Armstrong and Hilditch, 'Roy. Soc. Proc.,' A, vol. 96, p. 325 (1919).

† *Cf.* Armstrong and Hilditch, 'Roy. Soc. Proc.,' A, vol. 96, p. 142 (1919) and vol. 108, p. 123 (1925); Hilditch and Moore, 'J. Soc. Chem. Ind.,' vol. 42, p. 15 T (1923).

Since precise methods for the determination of the structure of polyethylenic aliphatic compounds are somewhat lacking, we have explored the possibility of utilising this procedure in the case of two polyethylenic acids whose constitution is fairly well established, namely, linoleic acid of soya bean or cotton-seed oil ($\Delta^{9:10,\ 12:13}$-octadecadienoic acid) and linolenic acid of linseed oil ($\Delta^{9:10,\ 12:13,\ 15:16}$-octadecatrienoic acid). We find that the process can be carried out quite smoothly, but the conclusions to be drawn from the acids isolated as scission-products from the oxidised oleic esters are complicated by the following factors:—

(i) Isomerisation occurs, ethylenic linkings appearing in positions adjacent to each original centre of unsaturation as described in the preceding paper, although to a less degree; since, for the most part, the ethylenic unions left in the semi-hydrogenated esters have taken no part in the actual hydrogenation.

(ii) The hydrogenation process is selective, not only as regards the degree of unsaturation present, but also to a considerable extent in that each ethylenic linkage is not equally attacked. Thus, in the case of methyl linolenate, the bond in the 15 : 16 position is most readily, and that in the 9 : 10 position least readily hydrogenated, with the result that the hydrogenated product (oleates) contains more of $\Delta^{9:10}$ and related isomers than of the $\Delta^{12:13}$ group, whilst the $\Delta^{15:16}$ products are present in smallest amount.

The increasing ease of hydrogenation of an ethylenic linkage as it is progressively more remote from the carboxylic group is a somewhat striking feature brought out by the present experiments. (Certain of our results suggest that the course of selective hydrogenation may vary with such conditions as the concentration of catalyst or the temperature employed;† whether a selection of conditions favourable to the production of suitable monoethylenic mixtures will thus become feasible remains to be determined by further investigation.)

Although it cannot be predicted (owing to the possibility of encountering too complex a mixture of oleic acids) that the method is capable in all cases of leading to definite conclusions, it is evident that the production of predominating proportions of respective pairs of monocarboxylic and dicarboxylic acids serves to determine the positions of corresponding unsaturated centres.

The utility and the present limitations of the procedure are illustrated by the experiments (about to be described) upon methyl linoleate and ethyl linolenate: we can deduce with certainty that the unsaturation in linoleic acid is in the 9 : 10 and 12 : 13 positions, whilst, in linolenic acid, we can fix the positions of the 9 : 10 and 12 : 13 linkages, but can only say that the third double bond lies beyond the fourteenth carbon atom of the chain.

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* Hilditch and Vidyarthi, *supra*, p. 552.

† *Cf.* also K. A. Williams, 'J. Soc. Chem. Ind.,' vol. 46, p. 446 T (1927).

The application of the process to polyethylenic branched-chain compounds is doubtless less complicated by isomerisation during hydrogenation, and, indeed, instances of its application to dihydrogeraniol and dihydrolinalool have already been given by E. F. Armstrong and one of us.*

It may be added that oxidation of a partially-hydrogenated product by means of ozone may, of course, be practised alternatively to our preferred method of treatment in hot acetone solution with anhydrous permanganate.

### *Esters of Linoleic and Linolenic Acid Studied.*

*Methyl Linoleate.*—(i) A specimen of the almost pure ester (iodine absorption, found 177·0 per cent., calc., 172·9 per cent.) was prepared by separating linoleic acid from the mixed acids of soya bean oil in the form of the crystalline tetrabromostearic acid, and reducing this with granulated zinc in 5N-methyl-alcoholic hydrogen chloride;† the resulting methyl linoleate was purified and distilled under diminished pressure.‡

(ii) From cottonseed oil, the mixed fatty acids were separated into saturated and unsaturated portions by the lead-salt method; the distilled methyl esters of the unsaturated acids (iodine absorption 130 per cent., equivalent to a composition of 49 per cent. oleate and 51 per cent. linoleate) were employed as such for the investigation.

*Ethyl Linolenate.*—This was prepared, from crystalline hexabromostearic acid obtained by addition of bromine to the mixed fatty acids of linseed oil in solution in ether, by reduction with zinc in boiling 5N-ethyl-alcoholic hydrogen chloride (the debromination is in this case effected but slowly in methyl alcohol solution). The iodine absorption of the distilled ester was 238·0 per cent. (calc. 249·0 per cent.).‡

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* 'Roy. Soc. Proc.,' A, vol. 108, p. 131 (1925).

† Rollett, 'Hoppe-Seyler's Z.,' vol. 62, p. 410 (1909).

‡ It is remarkable, in view of the ease of isomerisation of the higher unsaturated fatty acids under suitable conditions, that the somewhat drastic debromination process does not produce a mixture of linoleic (or linolenic) acids. We have, however, oxidised a portion of the product directly by the permanganate-acetone method, and were unable to detect any dicarboxylic acid other than azelaic acid, thus confirming the observations of other workers on the subject. *Cf.* Erdmann, Bedford and Raspe, 'Ber. d. Chem. Ges.,' vol. 42, p. 1334 (1909).

### *Partial Hydrogenation of the Esters.*

The esters were hydrogenated at 100–105° in order to minimise, since it was not possible to exclude, isomeric change; nickel on kieselguhr was, as before (*cf.* preceding paper, p. 556), used as catalyst, the concentration of nickel in the ester being about 0·3–0·6 per cent. Partially hydrogenated products were obtained as follows :—

| Ester. | Source of acid. | *g.* | Iod. absn. per cent. | Product hydrogenated approximately to— |
|---|---|---|---|---|
| Methyl linoleate .... | Soya bean oil .... | 81·5 | 85·7 | Monoethylenic stage (I.V. 85·8). |
| Methyl linoleate (+ oleate) | Cotton seed oil | 142·5 | 88·0 | Monoethylenic stage (I.V. 85·8). |
| Ethyl linolenate .... | Linseed oil ........ | 69 | 107·0 | Monoethylenic stage (I.V. 81·9). |
| ,, .... | ,, .... | 71 | 164·8 | Diethylenic stage (I.V. 164·9). |

The semi-hydrogenated esters were treated in 10 per cent. solution in acetone with powdered permanganate, and the products of oxidation were separated and examined in each case exactly as described in the preceding communication (p. 557). The various results thus obtained are summarised below for each of the four partially-hydrogenated mixtures.

### *Methyl Linoleate (from Soya Bean Oil), after Hydrogenation to the Monoethylenic Stage.*

The semi-hydrogenated ester (75 g.) gave, after oxidation (*a*) neutral material (12 g., iodine absorption 1·4 per cent.) and (*b*) acidic products which were separated into monocarboxylic acids (16 g.) and dicarboxylic acids (44 g.).

Dicarboxylic Esters.

| No. | *g.* | Equivalent. | Dicarboxylic acids identified. |
|---|---|---|---|
| 1 | 3·0 | 108·0 | Suberic, 139–140°; azelaic, 104–105°. |
| 2 | 10·3 | 105·1 | Suberic, 139–140°; azelaic, 104–105°. |
| 3 | 9·1 | 112·8 | |
| 4 | 4·4 | 119·2 | Undecane dicarboxylic, 110–111° (equivalent, found 108·0). |
| 5 | 3·4 | 123·0 | |
| 6 | 6·4 | 130·4 | Dodecane dicarboxylic 125–126° (125–126°*) (equivalent, found 115·2). |
| | 36·6 | | |

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* Melting-points in brackets are those of mixtures with authentic specimens—in this particular case with dodecane-dicarboxylic acid from partially-hydrogenated methyl erucate (preceding paper, p. 562).

Thus, the analysis of the dicarboxylic acids indicates that the main component of the methyl oleate mixture was $\Delta^{9:10}$- (with some $\Delta^{8:9}$ and probably $\Delta^{10:11}$)-octadecenoic acid, but that a notable amount of $\Delta^{12:13}$-octadecenoic acid (with some $\Delta^{11:12}$-acid, presumably formed therefrom by isomerisation) was also present.

Fractionation of the small amount of monocarboxylic esters available afforded a general confirmation of these results.

It is not easy to arrive, from the analytical figures, at any accurate estimate of the relative proportions of the $\Delta^{9:10}$- and $\Delta^{12:13}$-groups of acids, but it would appear that these are in the neighbourhood of two equivalents of $\Delta^{9:10}$- to one equivalent of $\Delta^{12:13}$-octadecenoic acids (reckoning $\Delta^{8:9}$- and $\Delta^{10:11}$-acids as emanating from a $\Delta^{9:10}$-linkage, and $\Delta^{11:12}$-acid as emanating from an original $\Delta^{12:13}$-linkage).

### *Methyl Linoleate + Oleate (from Cotton Seed Oil), after Hydrogenation to the Monoethylenic Stage.*

The hydrogenated product (127 g.) yielded on oxidation (*a*) neutral esters (10·6 g., iodine absorption 1·7 per cent.), and (*b*) acidic products which were resolved into monocarboxylic acids (31·2 g.) and dicarboxylic acids (76·4 g.).

Dicarboxylic Esters.

| No. | *g.* | Equivalent. | Acids identified. |
|---|---|---|---|
| 1 | 17·0 | 103·0 | Suberic, 139–140° (139–140°); azelaic, 102–103°. |
| 2 | 11·5 | 106·0 | |
| 3 | 10·7 | 111·6 | Azelaic, 102–103°.* |
| 4 | 4·7 | 120·3 | Dodecanedicarboxylic, 125–126°* (equivalent, found 115·2). |
| 5 | 4·5 | 121·0 | Dodecanedicarboxylic, 125–126°. |
| 6 | 8·8 | 132·0 | Dodecanedicarboxylic, 125–126°. |
| | 57·2 | | |

* Small quantities of another, less soluble, acid were also present in fraction 3, but could not be identified; in fractions 4 and 5 there was a more soluble acid present, which appeared to be azelaic acid, but could not be definitely characterised.

The small proportions of suberic ($C_8$) acid (which emanates from $\Delta^{8:9}$-octadecenoic acid produced from the linoleate) and the abundant amounts of azelaic acid observed in this instance are in consonance with the observation* that, during hydrogenation of a mixture of linoleate and oleate, the latter remains unchanged.

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* Moore, 'J. Soc. Chem. Ind.,' vol. 38, p. 324 T (1919).

Evidence confirming that from the dicarboxylic acids was afforded by the fractional distillation at atmospheric pressure of the methyl esters of the monocarboxylic acids; methyl hexoate and also methyl nononate were present in quantity, but no esters of acids lower than hexoic were observed.

### *Ethyl Linolenate (from Linseed Oil), after Hydrogenation to (approximately) Monoethylenic Stage.*

The hydrogenated product (68 g.) was oxidised in acetone as usual, but with ten times its weight of permanganate. The acidic products of oxidation (51 g.) were distilled in steam in order to effect the removal of monocarboxylic acids; the steam-distillate was exactly neutralised by caustic soda and concentrated to a very small bulk, after which the monocarboxylic acids were liberated by sulphuric acid. This departure from the usual procedure was in order to minimise loss of any acids of low molecular weight. Fractional distillation of the dimethyl dicarboxylic esters and of the free monobasic acids resulted as follows:—

Dicarboxylic Esters.

| No. | *g.* | B.p./0·5 mm. | Equivalent. | Acids identified. |
|---|---|---|---|---|
| | | ° | | |
| 1 | 6·7 | 83–93 | 100·4 | Suberic, 137–138° (137–138°). |
| 2 | 5·9 | 95–97 | 106·0 | Suberic, 137–138°; azelaic, 103–104°. |
| 3 | 3·9 | 97–107 | 112·0 | No individual acid could be isolated. |
| 4 | 4·2 | 107–120 | 119·1 | |
| 5 | 4·0 | 121–140 | 128·3 | Dodecanedicarboxylic, 121–122° (124–125°). |
| 6 | 2·0 | 140–145 | 135·7 | An acid, m.p. 112–113° (equivalent, found, 132·0); admixture with brassylic or dodecane dicarboxylic acids showed that it was neither of these; it appears from the equivalent to be a mixture of tetra- and penta-decane dicarboxylic acids. |
| 7 | 4·2 | Residue | 142·3 | No individual acid was identified. |
| | 30·9 | | | |

Monocarboxylic Acids.

| No. | *g.* | B.p./760 mm. | Equivalent. |
|---|---|---|---|
| | | ° | |
| 1 | 2·3 | 135–204 | 116 |
| 2 | 2·2 | Residue | 145 |

It is evident that partial hydrogenation of linolenic acid leads mainly to the formation of $\Delta^{9:10}$-oleic acids, whilst the $\Delta^{12:13}$-oleic acid is also produced in amounts readily detectable by the present method; but the quantity of the third isomeride is so small that the method is incapable of indicating more than that a dicarboxylic acid containing 14 or more carbon atoms is produced on oxidation. Similarly, the monobasic acids obviously include members lower than hexoic, but it is not possible to determine the individual lower acid present.

### *Ethyl Linolenate (from Linseed Oil), after Hydrogenation to the Diethylenic Stage.*

The partially hydrogenated ester (69 g.) yielded by oxidation 13 g. of monocarboxylic acids (separated by distillation in steam), and 31 g. of dicarboxylic acids.

Fractional Distillation of the Dicarboxylic Methyl Esters.

| No. | *g.* | B.p./0·5 mm. | Equivalent. | Acids identified. |
|---|---|---|---|---|
| | | ° | | |
| 1 | 5·5 | 70–89 | 97·2 | An acid, 130–135° (equivalent, found 85·7) mixed with suberic acid, 135–137°. |
| 2 | 10·1 | 89–91 | 104·0 | Suberic acid, 138–139°; azelaic acid, 103–104°. |
| 3 | 4·6 | 91–100 | 109·7 | |
| 4 | 3·5 | 105–120 | 119·0 | Dodecane dicarboxylic acid, m.pt. 125–126°. |
| 5 | 4·6 | Residue | 137·7 | |
| | 28·3 | | | |

Monocarboxylic Acids.

The free acids were distilled at atmospheric pressure:—

| No. | *g.* | B.p./760 mm. | Equivalent. |
|---|---|---|---|
| | | ° | |
| 1 | 1·8 | 130–160 | 82 |
| 2 | 2·3 | Residue | 135 |

The dicarboxylic acid scission products were again mainly azelaic and dodecane dicarboxylic acids, whilst the monocarboxylic compounds present included hexoic acid and an acid of molecular weight lower than 82 (butyric, 88; propionic, 74). The evidence given by this experiment therefore points clearly, again, to the presence of ethylenic linkages in the original ester in the

$\Delta^{9:10}$- and $\Delta^{12:13}$-positions, but it would have been difficult to assert definitely from the results obtained that the remaining unsaturated centre was at the $\Delta^{15:16}$-position.

### *Summary.*

Partial hydrogenation of esters of polyethylenic higher fatty acids to the monoethylenic state, followed by controlled disruptive oxidation of the products, is capable of giving useful information as to the position of the original ethylenic linkages, subject to the complications that (*a*) different ethenoid bonds are not usually hydrogenated at the same rate (so that there is disparity in the relative amounts of monoethylenic derivatives formed), and (*b*) the isomerisation phenomena discussed in the preceding communication are encountered (but to a less degree than in the hydrogenation of monoethylenic esters).

If the respective groups of mono- and di-carboxylic acid scission products eventually obtained are separately converted into methyl esters and fractionally distilled, the disturbing factors mentioned do not in general interfere seriously with the utility of the procedure as a means of determining the constitution of polyethylenic compounds.

We desire to acknowledge the assistance given to one of us (N.L.V.) by the Government of Bihar and Orissa during the course of this work.

# *Electron Scattering in Helium.*

By E. G. DYMOND, Fellow of St. John's College, Cambridge, and E. E. WATSON, Gonville and Caius College, Province of Quebec Scholar.

(Communicated by Sir Ernest Rutherford, P.R.S.—Received November 27, 1928.)

The work about to be described is a continuation of an investigation begun by one of us* at Princeton, New Jersey, on the scattering of electrons by gas atoms. The conditions there were so chosen that only single collisions were taken into account, and it was possible to investigate not only the energy loss on collision, as in the Franck and Hertz experiments, but also the direction of the path of the electron after collision.

By employing a magnetic analysis of the velocity of the electron after impact it was found possible to obtain information as to the probability of excitation of various stationary states of the atom considered, on collision with electrons of much higher velocities than could previously be used. The curves relating scattered intensity with angle of scattering were found to have sharp maxima, which were strongly suggestive of diffraction maxima, as might be expected if the motion of electrons is governed by the wave mechanics. But whereas the wave mechanics has been eminently successful in explaining the scattering results of Davisson and Germer† with single metal crystals, and of Thomson and Rupp‡ with thin metal foils the results of Dymond have been inexplicable on this basis. It may be said at once that we have been unable to find any trace of the sharp maxima found by him in I, which were apparently due to a secondary cause.§ Indeed, as has recently been pointed out by Elsasser,‖ no interference effects can be expected, when the electron loses energy on collision, the case in which Dymond found maxima, for the frequencies of the electron before and after interaction with the atom are different and there can consequently be no coherence of the scattered waves.

We must look therefore for interference effects in electrons which have been elastically reflected. As mentioned before such effects are not found to exist and the scattering curves resemble but do not coincide with those expected on classical considerations. The present work is substantially a repetition of that described in I. Attention has been concentrated on a narrow range of initial conditions and no attempt at an exhaustive enquiry has been made. Further work on the subject, particularly in the direction of lower initial velocities, and with various gases, is being continued.

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* Dymond, 'Phys. Rev.,' vol. 29, p. 433 (1927), hereafter described as I.

† 'Phys. Rev.,' vol. 30, p. 705 (1927).

‡ Thomson, 'Roy. Soc. Proc.,' A, vol. 117, p. 600 (1928) and vol. 119, p. 651 (1928); Rupp, 'Ann. Physik,' vol. 85, p. 981 (1928).

§ Harnwell, 'Proc. Nat. Acad. Sci.,' vol. 14, p. 564 (1928).

‖ 'Naturwiss.' September 14, 1928.

### *Apparatus.*

The design of apparatus follows closely that previously adopted, and is shown in figs. 1 and 2.

Electrons from a tungsten filament F are accelerated towards the side of a box G by an electric field. A narrow beam leaves the box by a slit $S_1$. The "gun" G can be rotated bodily about an axis perpendicular to the paper (fig. 1). Two fixed slits $S_2$ and $S_3$ select a beam of electrons which can only be derived from the initial beam by collisions with gas atoms along the axis; *i.e.*, they select electrons which have been scattered through an angle $\theta$. Low gas pressure insures that the probability that an electron may make two collisions between the slits $S_1$ and $S_2$ is small. To determine the velocity of the electrons after impact they are bent in a magnetic field and enter a Faraday cylinder K through the slit $S_4$.

In order to avoid further scattering of the beam and consequent reduction in intensity after it has passed the slits $S_2$ and $S_3$ the space D in which it moves under the action of the magnetic field is highly evacuated. Two fast diffusion pumps attached at H and J through wide tubing and low resistance mercury vapour traps pump off the gas as it leaks through the slits $S_2$ and $S_3$ from the space above and maintain a vacuum of $10^{-4}$ mm. or lower when the pressure in the collision space is $10^{-1}$ mm.

The collision chamber in which the electron "gun" is situated consists of a cylindrical tube, and the axis of rotation of the gun, which defines the point at which the collisions to be considered take place, is now in the centre of this tube, 8 mm. above the first receiving slit $S_2$, and 2 mm. from the slit $S_1$ of the gun. In the previous apparatus these measurements were approximately 1·5 mm. and 10 mm. The slit $S_1$ was 0·3 mm. wide, $S_2$ and $S_3$ were 0·1 mm. wide, and $S_4$ was variable, while the box was evacuated, by a device not shown, from 0 to 2 mm. It was used for the most part when 1 mm. wide.

In order to reduce stray effects due to electrons being scattered by the walls of the tube, this was lined with thin aluminium sheet at all points where the main beam of electrons might strike, and the lining was connected to the slit system. As the filament was connected to a negative potential and all the

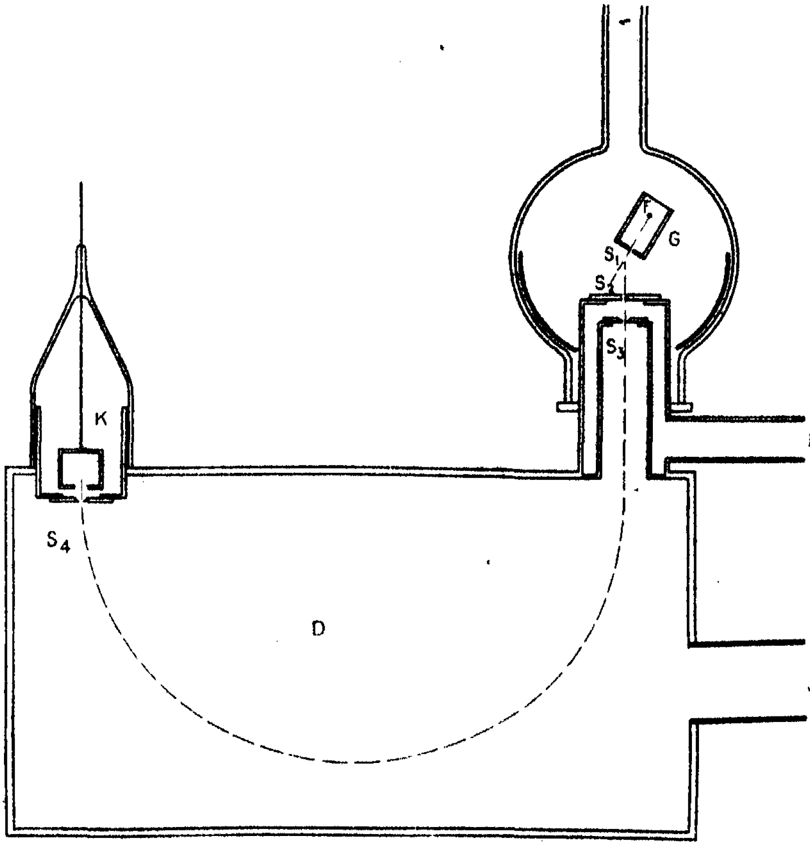

FIG. 1.—Apparatus. End View of Tube.

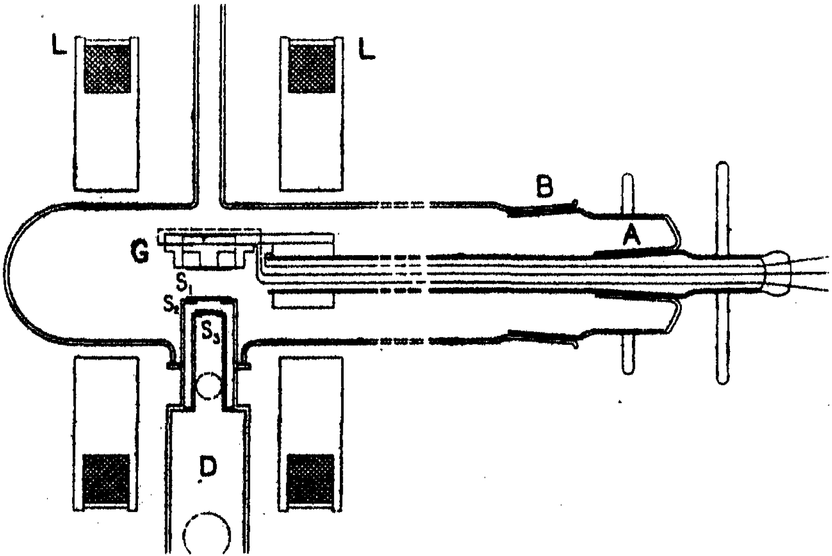

FIG. 2.—Apparatus. Side View of Tube.

slits were earthed, the space in which collisions occurred was free from electrostatic fields. The back of the gun was closed in, so that only electrons proceeding through the slit $S_1$ could find their way into the chamber. The "gun" G was mounted on a glass tube which could be rotated, the ground joint A being lubricated with rubber grease. The joint B permitted the withdrawal of the entire gun for adjustment and filament renewal and was used dry with a sealing of wax on the outside. The magnetic field was produced by two coils in the Helmholtz arrangement, not shown, with mean radius 20 cms. They produced a sensibly uniform field over the entire path of the electrons. In the region where collisions take place this field was compensated by two smaller coils L, also in the Helmholtz arrangement, of mean radius 7·3 cms., carrying a fixed proportion of the current in the main coils.

The earth's field was also compensated by two large coils, not shown, encircling the whole apparatus.

As previous experience had shown that the effects to be expected were very sharp, the current through the main coils was measured by a sensitive potentiometer connected across a low resistance in series with the coils. The current could be measured and held steady to 1 part in 5000. Similarly the voltage applied between the filament and slits, was stepped down by a fixed potential divider and was measured on the same potentiometer to the same degree of accuracy. The secondary cells supplying the accelerating potential could not maintain it constant to this degree, so that it was necessary to place in series with them a potential divider capable of applying increments of 0·02 volts.

The currents to the Faraday cylinder K were measured on a Compton quadrant electrometer. This was used with "positive" electrostatic control and was quite stable at the sensitivities used, from 5000 to 20,000 mm. per volt, at 1·5 metre scale distance.

The behaviour of this instrument as a means of measuring small currents has been examined in detail by one of us*. It appears that the current sensitivity is not proportional to the voltage sensitivity but approaches a maximum asymptotically. At the sensitivity most frequently employed a rate of drift of 1 mm. per second corresponded to a current of $10^{-14}$ amperes. There is practically no gain in working with higher voltage sensitivities and a distinct loss in ease and quickness of taking readings. The rate of drift was established to be exactly proportional to the current over a wide range.

The helium used was purified by prolonged circulation over charcoal cooled in liquid air and over hot copper oxide. It was admitted to the apparatus from the storage reservoir through an adjustable leak and a second charcoal tube. The adjustable leak, which was found very satisfactory in use, consisted of the stem of a clay pipe. The hole was plugged with sealing wax; the stem was inserted in a vertical position between the gas reservoir and the apparatus in such a way that it could be completely immersed in mercury, on the high pressure side, thus closing all communication between the two parts of the apparatus, or a variable length of the stem could be exposed.

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* Watson, 'Proc. Camb. Phil. Soc.,' *in the press.*

It is known that heated copper oxide is unable to remove the last traces of hydrogen from helium, but great purity of gas was not essential, as the method of magnetic analysis of the scattered beam enables a direct separation of the effect of impurities, whose energy states are all much lower than those of helium.

The gas pressure varied from 0·08 mm. to 0·12 mm. of mercury in different experiments. It was established that in this range scattering was proportional to gas pressure, and all results have been reduced to a standard pressure and standard sensitivity of the electrometer.

### *Discussion of Results.*

For any given initial velocity of the electrons the intensity of scattering depends on two variables, the velocity of the electrons after collision and the direction of their path. The complete results must therefore be represented by a diagram in three dimensions. In practice, we must hold one variable constant, and determine the behaviour of the other.

We will first discuss the results obtained when the angle of scattering is held constant and the velocity distribution of the electrons after impact is obtained by varying the magnetic field.

### *Velocity Distribution.*

Let $I(\theta, u)\, d\theta\, du$ represent the intensity of the scattered beam, reckoning the initial beam as unit intensity, between the limits $\theta$ and $\theta + \delta\theta$ of scattering angle and $u$ and $u + \delta u$ of velocity. This quantity will also be a function of the initial velocity $U_0$ of the electrons, but for the sake of simplicity we will consider $U_0$ constant for the moment. Then the current entering the Faraday cylinder will be proportional to

$$\delta\theta \int_{\alpha}^{\beta} I(\theta u)\, du$$

when the limits of integration are determined by the width of the slit $S_4$ in front of the Faraday cylinder. Let $\delta s$ be the width of this slit; then if $\rho$ be the radius of curvature of the electron beam when bent by the magnetic field H,

$$u \propto H\rho$$

and

$$du \propto H d\rho \propto H\delta s.$$

if $\delta s$ is small.

The current to the electrometer will consequently be proportional to

$$\delta\theta \int_{u - \delta u/2}^{u + \delta u/2} I(\theta u)\, du,$$

that is to say to

$$HI(\theta u)\,\delta\theta\,\delta s.$$

Consequently in order to determine the velocity distribution from the observed relation between electrometer current and deflecting field, we must divide each measured value by the relevant value of the magnetic field. As we are at the moment only interested in relative values, it is convenient to divide by the current in the field coils.

The velocity distribution for three initial velocities of 102, 226 and 386 volts, and for a scattering angle of 10° is shown in fig. 3. These curves may be

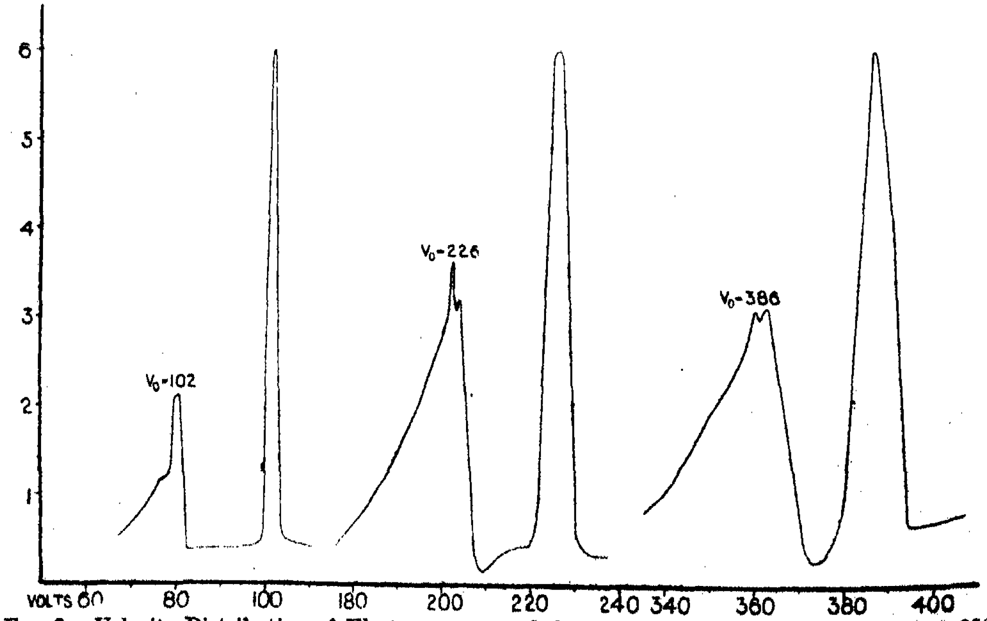

FIG. 3.—Velocity Distribution of Electrons scattered through 10° for initial velocities of 102, 226 and 386 volts.

compared with the curves shown in fig. 2 of I. No attempt has been made to obtain the sharp results there shown, which were made with fine slits and the best vacuum conditions in the analysing box D. For each curve, besides the peak corresponding to elastic collisions, two others appear, due to excitation and ionisation of the atom respectively. That due to excitation is compounded of several, representing the various energy states. It reaches its maximum value at 21 to 22 volts, which indicates that the excitation of the triplet system, which requires 19·8 volts, is very small or completely absent at these high velocities.

We see further that the effect of ionisation is at a maximum relative to that of excitation in the neighbourhood of 200 volts. This agrees with the result of Compton and Van Voorhis* who found that the efficiency of ionisation is at a maximum at about this velocity. As will be shewn later the efficiency of excitation is decreasing steadily throughout the range here investigated. The broadening of the " elastic " peak at the highest velocities is instrumental, due partly to poor vacuum conditions in the analysing chamber and partly to other causes not investigated.

The chief point of interest lies, however, in the further part of the curve, to which particular attention was drawn in I (p. 437). It was there found that at the higher initial velocities, the curve beyond the ionisation point did not drop down again, but even tended to rise ; it seemed that this was due to a higher probability that the atom could absorb energy continuously from a fast colliding electron, with a lower limit somewhere between the ionisation and first excitation states. This view was enlarged elsewhere† and discussed by Franck.‡

It can be seen at once that the continuous loss of energy in the curves under discussion here is much smaller than that found previously, and is substantially the same, relative to the loss due to excitation, at 382 volts as at 226 volts. There seems no reason in fact why it should not be attributed to the normal processes of ionisation. It is unfortunate, however, that no reason for the discrepancy between the two results can be found. It will be noted that whereas the curves shewn here are for a scattering angle of 10°, those in I are for an angle of 5°. But on repeating the observations at 5°, no difference in behaviour was noticed, whence it seems unlikely that the difference in angle can be made to account for the discrepancy. Nor does it seem likely that the somewhat higher pressure used in the present experiments should have any effect.

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* 'Phys. Rev.,' vol. 26, p. 436 (1925).

† Dymond, 'Proc. Camb. Phil. Soc.,' vol. 23, p. 804 (1927).

‡ Franck, 'Z. Physik,' vol. 47, p. 509 (1928).

### *Angular Distribution of Scattered Electrons.*

Let $I(\theta)\,\delta\omega$ represent the number of electrons scattered at an angle $\theta$ per unit solid angle per collision. Then it is easy to see that if the current we measure at any particular setting of the gun be $i(\theta)$

$$I(\theta)\,\delta\omega = C\,.\,i(\theta)\sin\theta.$$

For owing to the finite width of the beams, the number of collisions which any electron in the main beam can make is proportional to AB (fig. 4), which is proportional to cosec $\theta$. Also as the slit subtends a constant solid angle at the point of collision, $i(\theta)\sin\theta$ will be proportional to the scattering per unit solid angle. It should be noticed that in scattering experiments of $\alpha$ particles fired through thin foils, the angle between the incident beam and the scattering foil is constant, so that the number of atoms per square centimetre of the incident beam is constant.

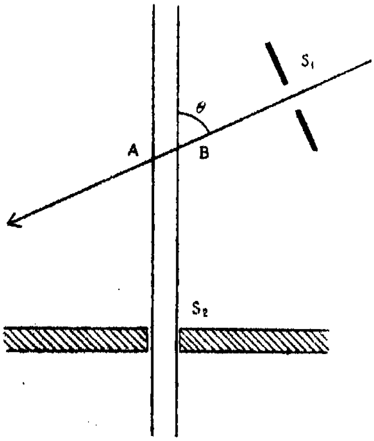

FIG. 4.

A typical set of results is shewn in fig. 5, which shews the scattering curves of both elastic and inelastic collisions, the latter corresponding to an energy loss of 21 volts, for a velocity of the primary electron beam of 210 volts. In order to eliminate stray effects a set of measurements with no gas in the tube was always taken immediately after a set with gas, and the difference was taken to represent the true gas scattering. This correction, which is due to secondary electrons from the slits, was vanishingly small in the case of inelastic impacts, and was never more than 25 per cent. for the elastic impacts. The ordinates represent the number of electrons scattered per unit solid angle per unit intensity of the primary beam. As will be seen, at large angles many more elastically reflected electrons occur than inelastically reflected electrons, while they approximate in number for smaller angles; in fact for higher initial velocities, *i.e.*, 400 volts, the inelastic group may considerably exceed the elastic group for 5° angle of scattering. To obtain the total number of scattered electrons in each group we must integrate each curve. There is an uncertainty in the extrapolation to zero angle, as the measurements become unreliable below 5°. But this uncertainty will not greatly affect the integrated result, especially as we notice that due to the sin θ correction term the curves cannot rise to infinite values for zero angle.

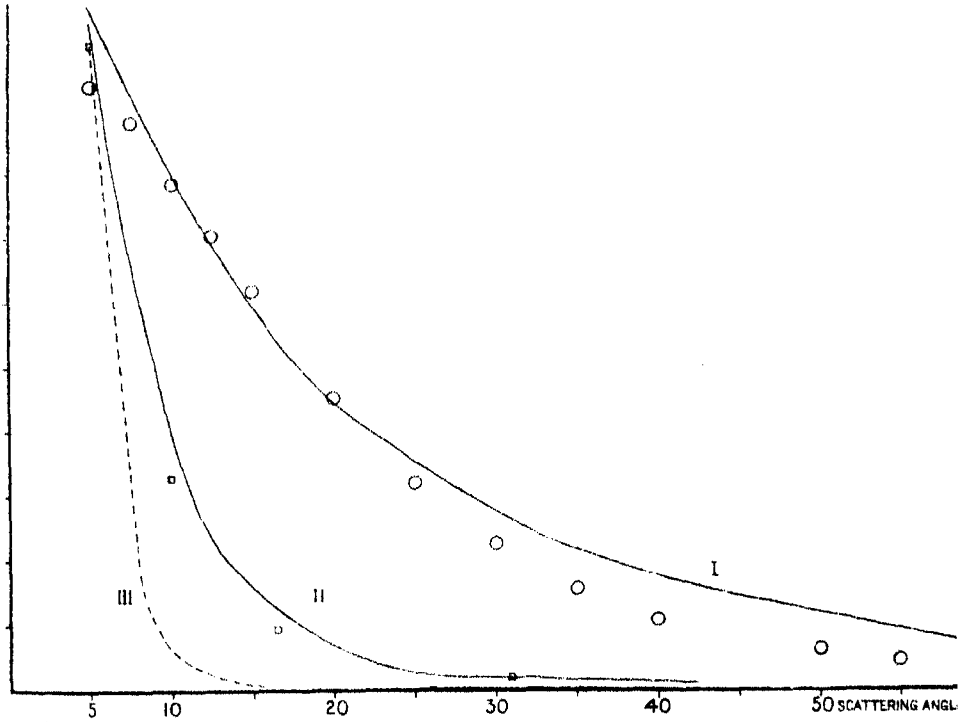

FIG. 5.—Angular distribution of scattered electrons for an initial velocity of 210 volts. I, Elastic collisions. II, Inelastic collisions (energy loss 21 volts). ○ Born's curve for elastic collisions in hydrogen. □ Curve calculated from the Hartree field. - - - - Inverse square law scattering curve.

On performing such integration we may tabulate the ratio of the elastic to the inelastic collisions for various electron velocities, V in volts.

| V. | Ratio $\frac{\text{inelastic}}{\text{elastic}}$ collisions. |
|---|---|
| 102 | 0·34 |
| 210 | 0·45 |
| 432 | 0·76 |

If we are justified in extrapolating these results to higher velocities it would seem that there may come a point where inelastic are more probable than elastic collisions. By comparing the areas for different velocities we can also see how the "target area" of the atom for collisions of the two kinds varies with velocity. The results are shown in fig. 6, where the target area for elastic collisions is arbitrarily taken as unity at 100 volts.

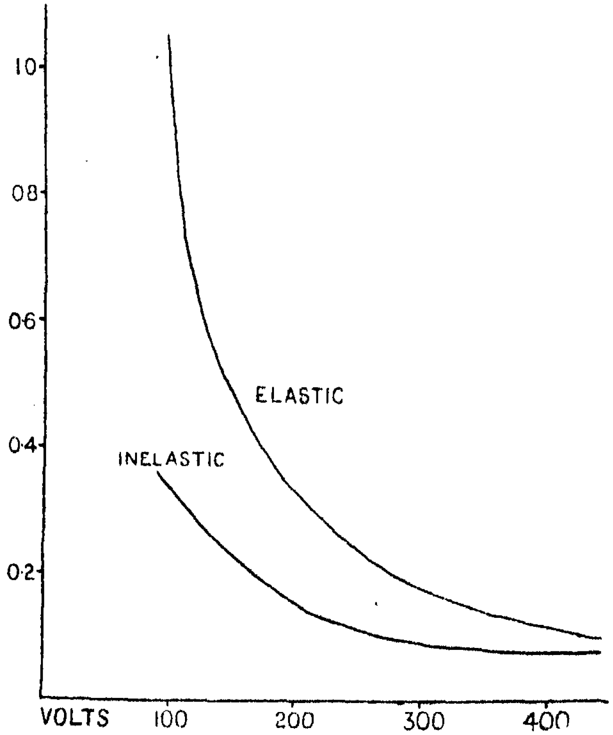

Fig. 6.—Relative Target Areas of the Helium Atom towards Electrons of different Velocities (elastic and inelastic impacts).

But of greater interest are the scattering curves themselves. By reducing to a common area and plotting we can see that their form does not vary much with velocity. As would be expected, there is a slight increase in steepness with increasing velocity, but this is not marked.

Let us now consider what form the scattering-curve may be expected to have from a theoretical standpoint. We will confine ourselves to the case of elastic reflection. Provided that the electron velocity is sufficiently high the only scattering agent will be the field of the nucleus, and the curve will be of the familiar kind associated with a Coulomb field and is represented by the function $\operatorname{cosec}^4 \theta/2$, where $\theta$ is the scattering angle. Any deviation that the experimental curve may show from this form must be ascribed to the influence of the orbital electrons of the atom.

A glance at fig. 5 will show that nuclear scattering calculated in this way is negligible, as might be expected from the comparatively low velocities employed. But we may get a closer approximation to the truth by assuming a certain mean field distribution in the atom (central but not Coulombian) and by determining the scattering that this field should produce. Hartree* has recently worked out the field of the helium atom from which by numerical integration the classical orbits of the impacting electrons may be determined and the scattering function found. But the result is again far from the truth, showing that a true quantum investigation of the case is required.†

For scattering in helium this has not been attempted, while for hydrogen Born‡ has achieved an approximate solution by means of the wave mechanics. His solution has been modified by Oppenheimer,§ but the additional terms of Oppenheimer to which numerical values cannot be assigned without a fuller investigation, are small in the region of velocities covered by this research.

While hydrogen and helium cannot be expected to yield identical scattering curves it is of interest to see that the hydrogen curve, when calculated for a somewhat smaller velocity (150 volts) than was experimentally used, fits closely. We do not wish to lay too much emphasis on this agreement, as the degree of fit may be adjusted by varying the velocity for which the hydrogen curve is calculated, but we would draw attention to the fact that the Born curve is the only one which in general shape at all resembles the experimental curve. That hydrogen and helium should have similar scattering properties when an adjustment of velocity is made to compensate for the greater field of the helium atom, is not contrary to expectation. It should be noted that the agreement referred to is only in the case of elastic impacts. The more complicated structure of helium, when the inelastic impacts are considered, introduces important divergences from the scattering calculated for hydrogen.

In conclusion a word should be said about the discrepancies between the results found in this work and in I. The note of Harnwell‖ previously referred to gives a clue. Using a much simplified apparatus he found sharp peaks in the scattering curves when the walls of his apparatus were glass, but that these peaks disappeared completely when the glass was covered with a conducting

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[*] 'Proc. Camb. Phil. Soc.,' vol. 24, p. 111 (1928). We are greatly indebted to Dr. Hartree for helpful advice at this point.

[†] This curve, of course, has nothing to do with the inelastic impact scattering curve with which it fortuitously coincides in this figure.

[‡] 'Göttinger Nachr.,' p. 146 (1926).

[§] 'Phys. Rev.,' vol. 32, p. 361 (1928).

[‖] Harnwell, *loc. cit.*

metallic layer. This would indicate that the peaks were due to a portion of the initial beam of electrons finding its way into the receiving slits by reflection at the charged glass walls, which may act almost as specular reflectors.

That some such effect was occurring in the measurements made in I is very probable, although the conditions seem to have been more complicated than in the experiments of Harnwell. In his case the peaks persisted when the gas was pumped out of the apparatus. In Dymond's experiments they disappeared simultaneously with the rest of the gas scattering, a fact which led to their confusion with the true scattering. While it is impossible to give a precise explanation of this behaviour, it is easy to see that the phenomenon is coupled with the occurrence of a positive ion space charge.

The peaks due to reflexion at the glass walls do not occur in the present work as it was arranged that the main electron beam always struck a metal surface.

In conclusion we wish to thank Prof. Sir Ernest Rutherford for his interest and advice in the research.

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# *On Bromine Chloride.*

By S. Barratt and C. P. Stein, University College, London.

(*Communicated by T. R. Merton, F.R.S.—Received November 29, 1928*).

It is curious, in view of the close attention which has been paid to many of the compounds formed between the halogens, that our knowledge of bromine chloride should be so vague that its very existence has frequently been denied. In 1826 Balard* described a compound between bromine and chlorine formed by direct union, and a few years later Loewig† claimed to have isolated a hydrate, $BrCl.5H_2O$, from solutions. Berthelot threw some doubt upon this early work‡ on account of the small heat of solution of chlorine gas in liquid bromine. Lebeau§ found that the crystals prepared in accordance with Balard's directions were variable in their composition and concluded from this and from the melting point curve of chlorine-bromine mixtures that no compound really exists. The same conclusion was reached by Karsten* and has been very generally adopted, except that the behaviour of bromine-chlorine mixtures in certain organic reactions, has occasionally led to suspicions of compound formation. One very cogent argument in favour of compound formation was touched upon by Balard, but has ever since been neglected—the marked diminution in the colour of bromine produced by admixture of chlorine. Our attention was drawn to this phenomenon by Mr. G. M. B. Dobson, of the Clarendon Laboratory, Oxford, who observed it in preparing filters for ultra-violet light from mixtures of the two gases† and who found further that the ultra-violet absorptions are not additive in these mixtures. It is with his kind permission that we have now investigated the matter more fully.

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* 'Ann. Chim. Phys.,' vol. 32, p. 371.

† 'Dissertation,' Heidelberg, 1829.

‡ 'Ann. Chim. Phys.,' vol. 21, p. 375 (1880).

§ 'C. R., vol. 143, p. 589 (1906).

The obvious explanation of the colour change is the formation of a compound between the two halogens, which is more transparent in the visible than is bromine ; though some physical influence of the chlorine on the bromine cannot immediately be ruled out as a hypothesis. The experiments described in the present communication were designed to test the chemical explanation, and to determine, if possible, the formula of the compound and the amount of it formed.

In order to estimate quantitatively the amount of bromine chloride formed, we made a spectrophotometric study of the absorption spectra of bromine and of bromine-chlorine mixtures. Our original intention was to work with the two materials in the vapour state, but in preliminary experiments we found that the same colour changes take place when the halogens are mixed in carbon tetrachloride solutions, and we have therefore used these solutions exclusively, as they are much more convenient for this type of optical measurement than are the vapours. Our conclusions are based upon the assumption that the intensity of the bromine absorption band in the visible forms a measure, in the mixtures, of the amount of bromine left uncombined with the chlorine. We had hoped to measure the chlorine left in the free state by similar observations on the ultra-violet bands, but, as will be seen later, this is not possible owing to the overlapping of the various spectra concerned (though the change can be followed qualitatively), and we had to be content with the "incomplete" photometric analysis of the mixtures. While this limitation detracts from the accuracy of the results, it does not affect the general conclusions. The original concentrations of bromine and chlorine before mixing were measured by ordinary chemical procedure (the liberation of iodine from potassium iodide) and these, along with the final concentration of bromine, deduced photometrically, provide sufficient data for testing the various equations possible for the reaction between the two elements, by means of their mass law constants.

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* 'Z. anorg. Chem.,' vol. 53, p. 315 (1907).

† *Cf.* also Peskov, 'J. Phys. Chem.,' vol. 21, p. 382 (1917).

*Quantitative Measurements on Colour Changes.*

The spectrophotometer with which these measurements were made was a Judd Lewis Sector Photometer, used in conjunction with a Hilger constant deviation spectrograph for work in the visible, and with an " E.3 " quartz instrument for the ultra-violet. The light source was a condensed spark from a kilowatt transformer, passing between electrodes of nickel steel, or of special tungsten steel. The carbon tetrachloride solutions of the halogens were held in glass tubes 10·3 cms. long fitted with quartz windows, cemented to the glass by zinc silicate. The main stocks of the bromine and chlorine solutions were kept in aspirators attached to burettes, and the air entering the aspirators was drawn through wash-bottles filled with solutions of the same strength as the main stock.

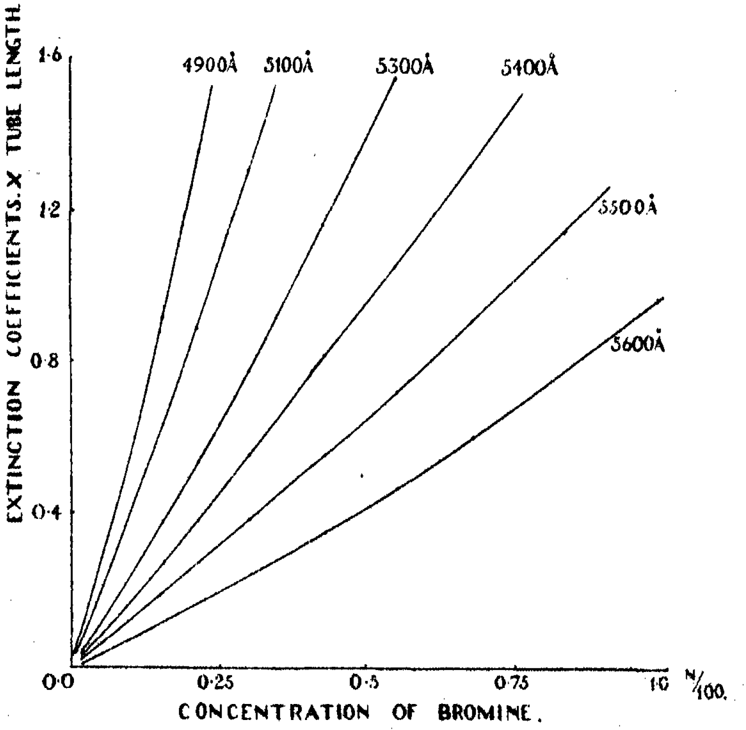

FIG. 1.

In a preliminary series of experiments the extinction coefficient of bromine was determined for wave-lengths between 4900 Å. and 5600 Å., over the range of concentrations necessary for the next series of measurements on the mixtures. In fig. 1 the "density" of 10·3 cms. of bromine solution (*i.e.*, extinction coefficient × tube length) is plotted against concentration, for each 100 Å. of the range. As can be seen, the curves are very flat, so that Beer's Law is approximately obeyed by the solutions, within the experimental range. The densities of solutions of bromine to which various proportions of chlorine had been added were afterwards determined. Some of the results are shown in fig. 2, in which density is plotted against wave-length. From these curves, together with those of fig. 1, it is possible to estimate the free bromine left in solution, uncombined with the chlorine. The means of the values so obtained are tabulated below, along with the original concentration of bromine and chlorine. If we assume that the bromine is removed to form BrCl in solution, then we can calculate the concentration of this compound which corresponds

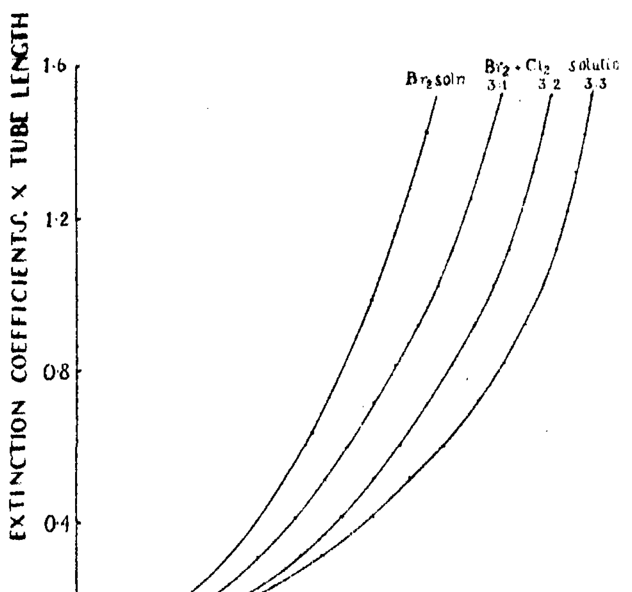

FIG. 2.

to the amount of bromine removed. These concentrations are also tabulated. Finally the reversible reaction

$$Br_2 + Cl_2 \rightleftarrows 2BrCl$$

should be governed by the equilibrium constant

$$[Br_2] \times [Cl_2]/[BrCl]^2 = K,$$

and the values of this "constant" are given in the last column. While the variations among them are considerable, it must be remembered that the analysis of the system is "incomplete," and that the accuracy with which the bromine concentration can be determined is certainly not greater than 2 per cent. by the optical method which we have used. Errors of this order are sufficient to account for the variations in the constant. We have calculated the corresponding equilibrium constants for other possible reactions, *e.g.*, the formation of $Br_2Cl_2$, $BrCl_3$, etc., and these all vary wildly. It would seem, therefore, that the colour changes on mixing bromine and chlorine solutions can be accounted for quantitatively on the basis of the formation of a compound BrCl, and that in equimolecular mixtures this compound is formed to the extent of approximately 50 per cent.

Table I.

| Total $Br_2$ × N/100. | Total $Cl_2$ × N/100. | Uncombined $Br_2$ × N/100. | Uncombined $Cl_2$ × N/100. | [BrCl] × N/100. | K. |
|---|---|---|---|---|---|
| 1·090 | 1·123 | 0·587 | 0·611 | 1·024 | 0·35 |
| 1·015 | 0·835 | 0·605 | 0·425 | 0·82 | 0·38 |
| 1·090 | 0·552 | 0·767 | 0·229 | 0·646 | 0·42 |
| 1·067 | 1·05 | 0·597 | 0·58 | 0·94 | 0·39 |
| 1·067 | 0·69 | 0·683 | 0·306 | 0·384 | 0·35 |
| 1·067 | 0·345 | 0·805 | 0·083 | 0·262 | 0·24 |
| 0·853 | 1·34 | 0·314 | 0·801 | 1·078 | 0·22 |
| 0·853 | 1·095 | 0·414 | 0·656 | 0·878 | 0·35 |
| 0·853 | 0·825 | 0·506 | 0·478 | 0·694 | 0·49 |
| 0·713 | 0·694 | 0·308 | 0·289 | 0·81 | 0·14 |
| 0·713 | 0·472 | 0·39 | 0·149 | 0·646 | 0·14 |
| 0·713 | 0·232 | 0·525 | 0·044 | 0·376 | 0·16 |
| 0·466 | 0·309 | 0·271 | 0·114 | 0·39 | 0·20 |
| 0·466 | 0·154 | 0·364 | 0·052 | 0·204 | 0·45 |
| 0·301 | 0·298 | 0·132 | 0·129 | 0·338 | 0·15 |
| 0·301 | 0·1993 | 0·175 | 0·073 | 0·252 | 0·20 |
| 0·301 | 0·0996 | 0·221 | 0·0196 | 0·16 | 0·17 |

### *Ultra-violet Absorption of Mixtures.*

We intended to supplement the equilibrium values given above by others deduced from similar measurements on the ultra-violet bands of both bromine and chlorine, in order to gain a direct check on the proportion of the latter entering into combination. Unfortunately this proved to be impossible, as the mixtures showed a new band in the gap between the bands of elementary bromine and chlorine. In fig. 3 the values of the extinction coefficients × tube length of bromine and chlorine, and of mixtures in the molecular ratio 1 : 1 and 1 : 3, have been plotted against wave-length.

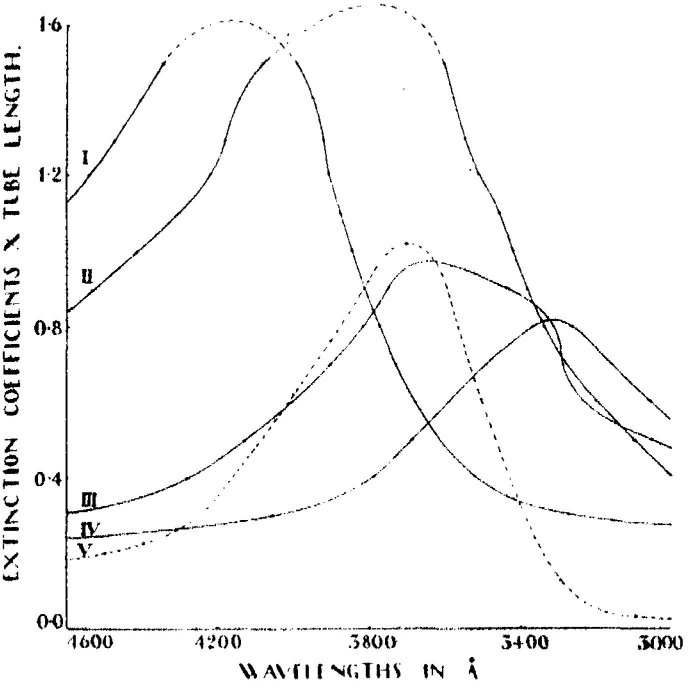

FIG. 3.

| | Concentration of $Br_2$. | Concentration of $Cl_2$. |
|---|---|---|
| I. | 1·1 N/1000 | — |
| II. | 1·1 N/1000 | 1·1 N/1000 |
| III. | 0·34 N/1000 | 1·1 N/1000 |
| IV. | — | 1·1 N/1000 |
| V. | Derived curve for BrCl. | |

We did not work with solutions of sufficient dilution for the matching of the maxima of two of the bands, as shown by the dotted part of the curves. The extra absorption shown by the mixtures is interesting confirmation of the formation in them of a new type of molecule, and from the results of the preceeding section we ascribe it to the molecule BrCl. A similar compound band appears in gaseous mixtures, and in aqueous solutions. Curve V shows the absorption of BrCl alone, derived from Curve II, by making allowance for the equilibrium concentrations of $Br_2$ and $Cl_2$, which can be calculated from the mass action constant, as given above.

The maximum evidently lies at 3700 Å.

### *Rate of Reaction.*

We have made a few preliminary observations on the rate of the colour change following the mixing of the two halogens. In solution in ether and chloroform the reaction seems to be completed immediately even at low temperatures such as $-78°$ C., nor have we been able to detect a " time lag " in colour on mixing aqueous solutions. In carbon tetrachloride, however, the lag is quite appreciable, and on mixing the solutions at room temperature the colour continues to diminish for several seconds. At the freezing point of the solvent the reaction is slower still, as would be expected. It is more difficult, by these crude observations, to test the rate in the gaseous state, but we suspect that here again the change takes an appreciable time to reach completion.

### *Summary.*

From spectrophotometric observations on the colour changes on mixing carbon tetrachloride solutions of bromine and chlorine, we conclude that in such solutions the two halogens combine to give an equilibrium concentration of bromine monochloride. In equimolecular mixtures about 50 per cent. of the halogens are present as the compound. The same type of colour change, and presumably the same chemical changes, occur when the halogens are mixed as gases, or as solutions in other solvents. The formation of a chemical compound between them is further indicated by the appearance of a new ultraviolet absorption band, with its maximum at 3700 A., peculiar to the mixtures, and also by the fact that the colour change in carbon tetrachloride solution takes an appreciable time, a phenomenon difficult to explain on any other basis than that of a slow reaction. The formula of the compound which is suggested above, agrees with the observation that on mixing chlorine and bromine in the gaseous state the volume change, if existent, is very small.

# *Perturbation Theory in Quantum Mechanics.*

By A. H. Wilson, Emmanuel College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received December 6, 1928.)

## 1. *Introduction.*

The theory of perturbations of electronic systems has been considered by various writers,* and the method is the basis of the solution of most quantum problems. It therefore seems desirable that the theory should be placed on a firm footing, and this necessitates the discussion of the convergence of the series of perturbations, which up to the present has been avoided. This investigation is all the more necessary since the wave equation of the Stark Effect has no solution of the form assumed by Schrödinger in his original discussion of the perturbation theory.

Dirac's theory leads to a system of linear differential equations in an infinite number of variables, and § 2 is devoted to the discussion of the existence theorem for such a system by a matrix method. In § 3 the application is made to the perturbation theory in the case of perturbations satisfying the conditions assumed in § 2. In § 4 the theory is extended so as to include more general types of disturbances. It is shown that, though the series of perturbations does not in general converge, yet it usually possesses the same asymptotic character as in the classical theory, and its use can therefore be justified.

Throughout the paper the investigation is limited to systems possessing only discrete spectra, and there is no obvious extension of the method to systems with continuous spectra.

## 2. *The Existence Theorem for a Differential System.*

We consider the infinite system of linear equations

$$\frac{dw_i}{dz} = \sum_{j=1}^{\infty} u_{ij} w_j \qquad (i = 1, 2, 3, \ldots)$$

where the coefficients $u_{ij}$ are functions of $z$. We shall obtain a solution of these equations, under certain conditions, by an extension of the Peano-Baker† method to an infinite number of variables.

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* Born, Heisenberg and Jordan, 'Z. Physik,' vol. 35, p. 557 (1926); Schrödinger, 'Ann. Physik,' vol. 80, p. 437 (1926); Dirac, 'Roy. Soc. Proc.,' A, vol. 112, p. 66 (1926).

† Peano, 'Math. Ann.,' vol. 32, p. 157 (1890); Baker, 'Phil. Trans.' A, vol. 216, p. 129 (1916). For a short account of the method see Ince, "Ordinary Differential Equations."

The system of equations may be written in the matrix form

$$\frac{dw}{dz} = uw, \tag{1}$$

where $u$ is the infinite matrix of the coefficients, and $w$ is the diagonal matrix $(w_1, w_2 \ldots)$. The problem is to find a system of solutions $w$, reducing to given values $w_0$ at a point $z_0$, such that $\sum_i |w_i|^2$ is finite provided that $\sum_i |w_i^0|^2$ is finite.

We assume that $z_0$ is not a singular point of any of the coefficients, and that it is possible to surround $z_0$ by a finite domain D free from singularities. We shall also assume that, throughout the whole of D, the matrix $u$ is limited in Hilbert's sense; that is, that the bilinear form $\left|\sum_{i,j=1}^{N} u_{ij} x_i y_j\right|$ is bounded for varying N, $x$, $y$, subject to the condition that $x_i$ and $y_j$ are any complex numbers satisfying $\sum_{i=1}^{\infty} |x_i|^2 \leqslant 1$, $\sum_{j=1}^{\infty} |y_j|^2 \leqslant 1$.

We shall also have occasion to use several well-known inequalities, and these are stated below so as not to interrupt the argument by reference to them.

Schwarz's inequality:

$$|\Sigma ab|^2 \leqslant \Sigma |a|^2 \,.\, \Sigma |b|^2.$$

Minkowski's inequality:

$$(\sum_n |\sum_m a_{mn}|^\kappa)^{1/\kappa} \leqslant \sum_m (\sum_n |a_{mn}|^\kappa)^{1/\kappa} \qquad (\kappa \geqslant 1)$$

and

$$\left(\sum_n \left|\int_E f_n(x)\, dx\right|^\kappa\right)^{1/\kappa} \leqslant \int_E (\sum_n |f_n(x)|^\kappa)^{1/\kappa},$$

where E is any measurable set.

Also

$$\Sigma |a+b|^\kappa \leqslant A_\kappa (\Sigma |a|^\kappa + \Sigma |b|^\kappa),$$

where $A_\kappa$ is a constant independent of $a$ and $b$. This can be extended to the sum of a finite number of terms $n$, with a constant $A_{\kappa,n}$, but not to an infinite number.

We define the matrix Q$u$ as the matrix whose elements are $\int_{z_0}^{z} u_{ij}(z)\, dz$, the integration being along any path lying in D. The symbol $u$Q$u$ denotes the matrix which is the product of the matrices $u$ and Q$u$. We write Q ($u$Q$u$) as Q$u$Q$u$, and so on. The series of matrices

$$\Omega(u) = 1 + Qu + QuQu + QuQuQu + \ldots \tag{2}$$

defines another matrix. We shall now prove that the matrix $\Omega(u)$ exists and is uniformly limited in the domain D.

The bilinear form corresponding to $Qu$ is limited if $u$ is limited. For

$$\left|\sum_{i,j=1}^{N}\int_{z_0}^{z} u_{ij}(z)\,dz\,x_iy_j\right| = \left|\int_{z_0}^{z}\sum_{i,j=1}^{N} u_{ij}(z)\,x_iy_j\,dz\right|$$
$$\leqslant \int_{z_0}^{z}\left|\sum_{i,j=1}^{N} u_{ij}(z)\,x_iy_j\right|dz \leqslant sM.$$

where M is a bound of the bilinear form $\sum_{ij} u_{ij}x_iy_j$, and $s$ is the length of the curve from $z_0$ to $z$ along which the integral is taken.

Also the bilinear form corresponding to $QuQu$ is limited, for

$$\left|\sum_{i,j=1}^{N}\int_{z_0}^{z}\sum_{r=1}^{\infty} u_{ir}(z)\,(Qu)_{rj}\,dz\,x_iy_j\right| = \left|\int_{z_0}^{z}\sum_{i,j=1}^{N}\sum_{r=1}^{\infty} u_{ir}\,(Qu)_{rj}\,x\,y_j\,dz\right|$$

and the product of two limited forms with bounds M and M′ is limited with bound MM′.

The last expression is therefore less than

$$\int_0^s M^2t\,dt = \frac{1}{2!}M^2s^2.$$

It is easily seen by induction that the bilinear form $\sum_{ij}\Omega_{ij}x_iy_j$ is limited with bound

$$1 + Ms + \frac{1}{2!}M^2s^2 + \dots = e^{sM},$$

and is therefore uniformly limited in D.

Consider the expression

$$w = (1 + Qu + QuQu + QuQuQu + \dots)\,w_0. \tag{3}$$

Differentiating term by term we have

$$\frac{dw}{dz} = (u + uQu + uQuQu + \dots)\,w_0 = uw.$$

The term by term differentiation is justified since

$$\begin{aligned}|w_i| &= |\textstyle\sum_j \Omega_{ij}w_j^0|\\ &\leqslant \{\textstyle\sum_j |\Omega_{ij}|^2 \,.\, \sum_j |w_j^0|^2\}^{\frac{1}{2}}\\ &= \{\textstyle\sum_j |\Omega_{ij}|^2\}^{\frac{1}{2}} \quad \text{if} \quad \textstyle\sum_j |w_j^0|^2 = 1,\end{aligned}$$

and the sum of the squares of the moduli of the elements of any row or column of a limited matrix is finite. The series is therefore uniformly and absolutely convergent.

We have thus proved that a solution of the differential equations is given by

$$w = \Omega(u)\, w_0.$$

Moreover, when $z = z_0$, $w$ reduces to $w_0$. We have yet to prove that $\sum_i |w_i|^2$ is finite.

Consider $\sum_{i,j=1}^{N} \Omega_{ij} x_i y_j$ as the linear form $\sum_{i=1}^{N} \left( \sum_{j=1}^{N} \Omega_{ij} y_j \right) x_i$. Then

$$\left| \sum_{i=1}^{N} \left( \sum_{j=1}^{N} \Omega_{ij} y_j \right) x_i \right| \leqslant \left\{ \sum_{i=1}^{N} \left| \sum_{j=1}^{N} \Omega_{ij} y_j \right|^2 \right\}^{\frac{1}{2}} . \left\{ \sum_{i=1}^{N} |x_i|^2 \right\}^{\frac{1}{2}} .$$

The sign of equality can be made to hold by choosing

$$|x_i|^2 = c \left| \sum_{j=1}^{N} \Omega_{ij} y_j \right|^2 \quad \text{where} \quad c = \sum_{i=1}^{N} |x_i|^2 \Big/ \left\{ \sum_{i=1}^{N} \left| \sum_{j=1}^{N} \Omega_{ij} y_j \right|^2 \right\},$$

and

$$am . \left\{ x_i \left( \sum_{j=1}^{N} \Omega_{ij} y_j \right) \right\} = \text{constant for all } i.$$

But the bilinear form is limited, and so

$$\sum_{i=1}^{\infty} \left| \sum_{j=1}^{\infty} \Omega_{ij} y_i \right|^2 \quad \text{is bounded if} \quad \sum_{j=1}^{\infty} |y_j|^2 \leqslant 1.$$

Therefore $\sum_{i=1}^{\infty} |w_i|^2$ is finite provided $\sum_{i=1}^{\infty} |w_i^0|^2$ is finite.

For a system of finite solutions $w$, it is necessary and sufficient that the sums $\sum_{j=1}^{\infty} |\Omega_{ij}|^2$, $(i = 1, 2, \ldots)$ should exist and be finite. For

$$|w_i| \leqslant \{\sum_j |\Omega_{ij}|^2 . \sum_j |w_j^0|^2\}^{\frac{1}{2}} \leqslant \{\sum_j |\Omega_{ij}|^2\}^{\frac{1}{2}}$$

and $|w_i|$ does attain its upper bound $\{\sum_j |\Omega_{ij}|^2\}^{\frac{1}{2}}$. This condition does not ensure that $\sum_i |w_i|^2$ is finite, though it is obviously a necessary condition for the last occurrence.

*Theorem.*—The necessary and sufficient condition that the system of equations $\frac{dw}{dz} = uw$ should have a solution for which $\sum_i |w_i|^2$ is finite in D, is that the matrix $\Omega(u)$ should be limited in D.

The condition is obviously sufficient, as we have proved the existence of such a solution when the condition is satisfied. The condition is also necessary, for we have by hypothesis that $\sum_i |w_i|^2 = \sum_i |\sum_j \Omega_{ij} w_j^0|^2$ is finite in D. But $|\sum_{ij} \Omega_{ij} x_i y_j| \leqslant \{\sum_i |\sum_j \Omega_{ij} y_j|^2\}^{\frac{1}{2}}$ and the matrix $\Omega(u)$ is therefore limited in D.

If the matrix $u$ is Hermitian then $\sum_i |w_i|^2 = \sum_i |w_i^0|^2$. The adjoint system of equations is

$$\frac{d\tilde{w}}{dz} = - \tilde{u}\tilde{w},$$

where $\tilde{u}$ is the transposed matrix of $u$.

Consider the expression $\frac{d}{dz}\{\sum_i w_i \tilde{w}_i\}$. We may differentiate term by term on account of the uniform convergence of the resulting series.

$$\begin{aligned}\frac{d}{dz}\{\sum_i w_i \tilde{w}_i\} &= \sum_i \frac{dw_i}{dz}\tilde{w}_i + \sum_i w_i \frac{d\tilde{w}_i}{dz} \\ &= \sum_{ij} \{u_{ij} w_j \tilde{w}_i - \tilde{u}_{ij} \tilde{w}_j w_i\} = 0.\end{aligned}$$

Therefore $\sum_i w_i \tilde{w}_i$ is constant and equal to $\sum_i w_i^0 \tilde{w}_i^0$. If $u$ is Hermitian then the adjoint matrix is equal to the conjugate complex matrix, and $w$, $\tilde{w}$ are conjugate. So

$$\sum_i |w_i|^2 = \sum_i |w_i^0|^2.$$

### 3. *Application to the Theory of Perturbations.*

We consider the perturbation theory introduced by Dirac.* Let the wave equation for the undisturbed system be

$$\left(\mathrm{H} - i\frac{h}{2\pi}\frac{\partial}{\partial t}\right)\psi = 0, \tag{4}$$

where H is independent of the time. Its general solution is

$$\psi = \sum_n c_n \psi_n,$$

where the coefficients are constants. If a perturbation is added at time $t = 0$, the wave equation becomes

$$\left\{\mathrm{H} - \frac{ih}{2\pi}\frac{\partial}{\partial t} + \mathrm{A}(t)\right\}\psi = 0. \tag{5}$$

Assuming a solution of the form

$$\psi = \sum_n a_n(t)\,\psi_n,$$

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* *Loc. cit.*

the $a_n$'s are given by the equations

$$i\frac{h}{2\pi}\dot{a}_m = \sum_n a_n \mathrm{A}_{mn}, \tag{6}$$

where $\mathrm{A}_{mn}$ is defined by the relation

$$\mathrm{A}\psi_n = \sum_m \mathrm{A}_{mn}\,\psi_m. \tag{7}$$

$\mathrm{A}_{mn}$ is a function of $t$ only, and the matrix $(\mathrm{A}_{mn})$ is Hermitian. If the matrix $\frac{2\pi}{ih}(\mathrm{A}_{mn})$ be denoted by $u$, and if $u$ is limited in $(0, t)$, then the general solution of the equations is

$$a_m = \sum_n \{1 + \mathrm{Q}u + \mathrm{Q}u\,\mathrm{Q}u + \ldots\}_{mn}\,c_n, \tag{8}$$

or as we may write it

$$a_m = \sum_{n=0}^{\infty}\left\{\sum_{r=0}^{\infty}(\mathrm{Q}u)^r\right\}_{mn} c_n. \tag{9}$$

The solution of equation (5) can also be put in the form

$$\psi = \sum_n c_n\phi_n(t),$$

where $c_n$ is a constant and $\phi_n(t)$ reduces to $\psi_n$ at time $t = 0$. $c_n$ must, therefore, be the same as in equation (8). If A contains a parameter $\lambda$, $\phi_n(t)$ can be arranged in powers of $\lambda$:

$$\phi_n(t) = \sum_{r=0}^{\infty}\phi_n^{(r)}(t).$$

where $\phi_n^{(r)}(t)$ contains $\lambda^r$.

It is permissible to equate powers of $\lambda$, and since $c_n$ is also arbitrary, we have

$$\phi_n^{(r)}(t) = \sum_{m=0}^{\infty}\{(\mathrm{Q}u)^r\}_{mn}\,\psi_m. \tag{10}$$

We can therefore express the solution of (5) in either of the two equivalent forms

$$\psi = \sum_m a_m(t)\,\psi_m;\quad a_m(t) = \sum_{n=0}^{\infty}\left\{\sum_{r=0}^{\infty}(\mathrm{Q}u)^r\right\}_{mn} c_n, \tag{11}$$

$$\psi = \sum_m c_m\,\phi_m(t);\quad \phi_m(t) = \sum_{n=0}^{\infty}\left\{\sum_{r=0}^{\infty}(\mathrm{Q}u)^r\right\}_{nm}\psi_m, \tag{12}$$

where Q is the operator $\int_0^t dt$ and $(\mathrm{Q}u)^r$ must be interpreted from equations (8) and (9). Also since $\psi_m$ is normalised, so is $\phi_m(t)$; and in addition the functions $\phi_m(t)$ form a complete system of orthogonal functions.*

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* Fock, 'Z. Physik,' vol. 49, p. 323 (1928).

### 4. *Extension to More General Perturbations.*

We have so far only dealt with perturbations whose matrix is limited. Most of the problems which arise in quantum mechanics involve unlimited matrices. By the theorem proved in § 2 there will no solution of the differential equations which satisfies all the conditions. It is still possible, however, to interpret the formal solution so as to give consistent results. All the matrices which occur in the perturbation theory have the property that the sum of the squares of the moduli of the elements of any row or column is finite. In this section, we examine the formal solution under this restriction.

It may happen that the number of elements in any row or column of the matrix $u$ is finite. This seems to be the case for most perturbations when the problem has only one degree of freedom, and also when the problem is separable as in the Stark Effect. We shall therefore examine this particular case.

We have

$$\sum_{r=1}^{\infty} |u_{ir}|^2 < \mathrm{M}^2, \qquad \sum_{r=1}^{\infty} |u_{rj}|^2 < \mathrm{M}^2 \qquad (i, j \leqslant \mathrm{N}),$$

where M is a constant depending on N.

Then

$$\begin{aligned}\left\{\sum_{r=1}^{\infty} |u_{ir}^{(1)}(z)|^2\right\}^{\frac{1}{2}} &= \left\{\sum_r \left|\int_{z_0}^{z} u_{ir}(z)\, dz\right|^2\right\}^{\frac{1}{2}} \\ &\leqslant \int_0^s (\sum_r |u_{ir}|^2)^{\frac{1}{2}}\, ds \\ &\leqslant \mathrm{M}s\end{aligned}$$

and

$$\begin{aligned}\left\{\sum_{r=1}^{\infty} |u_{ir}^{(2)}(z)|^2\right\}^{\frac{1}{2}} &= \left\{\sum_r \left|\int_{z_0}^{z} \sum_n u_{in}u_{nr}^{(1)}\, dz\right|^2\right\}^{\frac{1}{2}} \\ &\leqslant \int_0^s (\sum_r |\sum_n u_{in}u_{nr}^{(1)}|^2)^{\frac{1}{2}}\, ds \\ &\leqslant \kappa \int_0^s \{\sum_n \sum_r |u_{in}u_{nr}^{(1)}|^2\}^{\frac{1}{2}}\, ds,\end{aligned}$$

since the sum with regard to $n$ is a sum over a finite number of terms.

So

$$\left\{\sum_{r=1}^{\infty} |u_{ir}^{(2)}(z)|^2\right\}^{\frac{1}{2}} \leqslant \frac{1}{2\,!}\kappa \mathrm{M}^2 s^2,$$

and by induction

$$\left\{\sum_{r=1}^{\infty} |u_{ir}^{(m)}(z)|^2\right\}^{\frac{1}{2}} \leqslant \frac{1}{m\,!}\kappa^{m-1}\mathrm{M}^m s^m \qquad (m \leqslant m_0(\mathrm{N})).$$

where $\kappa$ and M depend on N.

Now consider the solution (8) with a remainder. It is

$$w = \{1 + \mathrm{Q}u + \mathrm{Q}u\,\mathrm{Q}u + \ldots + (\mathrm{Q}u)^n + \mathrm{R}_n\}\, w_0. \tag{13}$$

where

$$\mathrm{R}_n = e^{\mathrm{Q}u}\mathrm{Q}\,\{e^{-\mathrm{Q}u}u\,(\mathrm{Q}u)^n\}.$$

$e^{\mathrm{Q}u}$ is merely the matrix $e^{\int_{z_0}^{z} u\,dz}$ and is not to be expanded as a symbolical operator.

We further suppose that the perturbation A contains a small parameter $\lambda$, and therefore that $\mathrm{R}_n$ is divisible by $\lambda^{n+1}$.

Now $|\sum\limits_r \{1 + \mathrm{Q}u + \ldots + (\mathrm{Q}u)^n\}_{ir} w_r^0|$ is finite by the inequalities proved above, and $|\sum\limits_r (\mathrm{R}_n)_{ir}\, w_r^0|/\lambda^{n+1}$ is less than a constant depending on $n$, but independent of $\lambda$. Therefore for fixed $n$,

$$|w_i - \sum_r \{1 + \mathrm{Q}u + \ldots + (\mathrm{Q}u)^n\}_{ir}\, w_r^0|/\lambda^n = \mathrm{O}\,(\lambda) \rightarrow 0 \text{ as } \lambda \rightarrow 0.$$

This is just the condition that the solution

$$w = \Omega\,(u)\, w_0$$

should be an asymptotic series.

Thus the series

$$w_i = \sum_r \{1 + \mathrm{Q}u + \mathrm{Q}u\,\mathrm{Q}u + \ldots\}_{ir}\, w_r^0,$$

gives an asymptotic representation of the solution for all finite values of $i$, in just the same way that Poincaré's solution of the perturbation problem in classical mechanics is asymptotic. The justification of the use of such series is the same for both the quantum and classical theories.

## 5. *Periodic Solutions.*

We now consider a perturbation which is constant for $t \geqslant \mathrm{T}$. When $t \geqslant \mathrm{T}$, the total energy is a constant of integration of the system and can therefore be represented as a diagonal matrix. This means that a solution of the wave equation is possible in which the wave function only involves the time through the factor $e^{-\frac{2\pi i \mathrm{W}t}{h}}$, and is therefore a periodic solution for $t \geqslant \mathrm{T}$. Now the wave functions for the unperturbed system involve the time in the manner $\psi_n \propto e^{-\frac{2\pi i \mathrm{W}_n t}{h}}$. By the theorem on the existence of a solution, it must be possible to satisfy the wave equation of the perturbed problem by a series

$$\psi = \sum_n a_n \psi_n$$

where, for $t \geqslant \mathrm{T}$, $a_n$ only involves the time through the factor $e^{-\frac{2\pi i t}{h}(\mathrm{W} - \mathrm{W}_n)}$.

By considering an adiabatic perturbation we can obtain equations for W by equating the time factor in the solution of § 3 to $e^{-\frac{2\pi i t}{h}(W-W_n)}$; but the equations are in a very inconvenient form. We may evade the difficulty by substituting $a_n = b_n e^{-\frac{2\pi i t}{h}(W-W_n)}$ directly in the differential equations for $a_n$. We know that a solution is possible and therefore it must be given in this form, where $b_n$ is constant. There are an infinite number of linear equations for the $b_n$'s.

$$(W_n - W)\, b_n + \sum_m b_m B_{nm} = 0, \tag{14}$$

where

$$B_{nm} = A_{nm} e^{-\frac{2\pi i t}{h}(W_n - W_m)},$$

and is independent of the time. Assuming that the matrix

$$\left(\delta_{nm} - \frac{B_{nm}}{W - W_n}\right)$$

is limited, these equations are soluble if W is a characteristic of the matrix. If the perturbation involves a parameter $\lambda$, we may assume solutions in powers of $\lambda$, and equate coefficients. This leads to the perturbation theories of Born, Heisenberg, Jordan and Schrödinger. Even if the matrix is not limited, the formal solution will be asymptotic provided the less stringent conditions of § 4 are satisfied. We have already obtained, in § 3 equation (10), Schrödinger's solution for perturbations involving the time explicity, and it is now seen that all the perturbation theories are equivalent, as they ought to be.

We shall now show that the Stark Effect can be treated by this method. When the problem is separated in parabolic co-ordinates, the following equation arises[*]

$$\frac{d^2y}{dx^2} + \frac{n_3 + 1}{x}\frac{dy}{dx} + \left(Fx - \tfrac{1}{4} + \frac{\alpha}{x}\right) y = 0, \tag{15}$$

F is the perturbing term and $n_3$ is a positive integer or zero. For simplicity we shall put $n_3$ zero. When $F = 0$ the solutions of (15) are given by

$$y_n = e^{-x/2} L_n(x)$$

and

$$\alpha = n \qquad (n = 0, 1, 2, \ldots),$$

where

$$L_n(x) = e^x \frac{d^n}{dx^n}(x^n e^{-x}).$$

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[*] Schrödinger, *loc. cit.*

The matrix components of the perturbing energy are

$$B_{mn} = \frac{\int_0^\infty F x^2 e^{-x} L_m(x) L_n(x)\, dx}{\left\{ \int_0^\infty e^{-x} L_m^2(x)\, dx \,.\, \int_0^\infty e^{-x} L_n^2(x)\, dx \right\}^{\frac{1}{2}}}.$$

If we assume a solution of the perturbed equation in the form

$$y = \sum_n b_n y_n,$$

then

$$(n - \alpha) b_n + \sum_m b_m B_{nm} = 0.$$

Since $B_{nn} = 2F(3n^2 + 3n + 1)$, the matrix $\left(\delta_{nm} - \frac{B_{nm}}{\alpha - n}\right)$ is not limited; but, on account of the recurrence relation between three consecutive $L_n$'s,

$$L_{n+1}(x) - (2n + 1 - x) L_n(x) + n^2 L_{n-1}(x) = 0,$$

$B_{nm}$ vanishes unless $|m - n| \leqslant 2$. There will, therefore, be a solution, but only an asymptotic one. This is not a defect in the theory, but is a necessary feature. If there were an exact solution, $y$ would behave like $e^{-x/2}$ at infinity. This is impossible, as $Fx$ is the leading term at infinity. There is therefore no stationary state of the system. The theory developed here shows that the Stark Effect can be obtained by starting with a hydrogen atom initially, and then building up an electric field. Also, since the solution is only asymptotic, the electron cannot always stay in a quantised orbit under the action of the limiting electric field, however small, but must finally escape from the atom and become free.

This justifies Schrödinger's treatment of the Stark Effect to some extent, but there is still one point which requires to be considered. We have neglected the continuous spectrum of the system, and this is not really permissible as the electric field will induce transitions from the discrete states to the continuous states. Schrödinger avoids this difficulty by employing a transformation which has the effect of eliminating the continuous spectrum, thus obtaining equation (15). We have seen that there are no exact solutions of this equation, and this seems to correspond to the neglect of the continuous spectrum. It is therefore possible that a perturbation theory which included the continuous spectrum would be exact; but the present method seems inadequate to deal with such a theory.

In conclusion we have shown that, for a certain limited type of perturbation, the solution is asymptotic; but it may well happen that the solution is asymptotic in many other cases.

# *Effect of Combined Electric and Magnetic Fields on the Helium Spectrum.*[*]

By J. STUART FOSTER, Assistant Professor of Physics, McGill University.

[PLATE 10].

(Communicated by A. S. Eve, F.R.S.—Received October 24, 1928.)

*Introduction.*—This paper deals with the observed effect of simultaneous electric and magnetic fields on certain of the more intense helium lines, and is further limited to the case where the fields are uniform and parallel.

The effect of parallel fields was first considered by Garbasso,[†] who adopted the classical view of the "rough" Stark-effect on $H_\beta$ as given by Voigt,[‡] and concluded that the effects due to the two fields should be simply superimposed. Shortly after this he was able to make visual observations[§] which were restricted to $H_\alpha$ owing to intensity requirements. A source of the Lo Surdo type was placed along the axis of the hollow poles of a Weiss magnet, and the analysis made with a Michelson echelon. In the electric field alone Garbasso observed two parallel components and one undisplaced perpendicular component. This corresponds to a so-called "rough" analysis of the Stark-effect in which the individual components are not observed. In the magnetic field he found a normal Zeeman pattern. With combined parallel fields there appeared two parallel components in the position of the Stark components of like polarisation, and two symmetrically placed perpendicular components with the normal Zeeman separation. This simple result could not be given a satisfactory interpretation on classical theory.

The more adequate quantum theoretical solution of this problem was first given by Prof. Bohr,[||] who pointed out that the uniform Larmor precession of the electron orbit round an axis through the hydrogen nucleus and parallel to the applied fields does not affect the time mean displacement of the electron in the direction of this axis. That is, the application of a magnetic field does not influence the change in potential energy which resulted from a previously applied electric field. While this is in agreement with Garbasso as regards the independence of the Stark and Zeeman effects, the quantum theory gives

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[*] This research was assisted by a grant from the National Research Council of Canada.

[†] 'Ital. Fis. Soc.,' Florence, April, 1914.

[‡] 'Gott. Nachr.,' vol. 1, p. 71 (1914).

[§] 'Physik. Z.,' vol. 15, p. 729 (1914).

[||] 'On the Quantum Theory of Line Spectra,' Copenhagen (1922).

the correct number of components, and, in its latest form, the intensities as well. In the theoretical combined effect of parallel fields, each parallel Stark component remains unaffected by the magnetic field, while each perpendicular Stark component is split symmetrically into two components of equal intensity. The more recent theoretical developments by Epstein, Halpern, Klein, Urey and Pauli do not affect the interpretations of the data under discussion.

It is interesting to consider certain finer details of the above-mentioned experiment in the light of present theory. Given the correct number of Stark components of $H_\alpha$ with intensities as calculated by Schrödinger,[*] we still need to know the relative intensities of the two fields in order to complete a theoretical representation of the splitting in simultaneous parallel fields. Assuming that the displacements were represented on a common scale by Garbasso, it follows that the observed displacement of each perpendicular Zeeman component in the normal effect was very nearly equal to the theoretical unit in the Stark displacements at the electric field employed. On this basis it is not unreasonable to expect a moderately strong undisplaced perpendicular component which has not been found.

Such difficulties in regard to detailed interpretation arise partly from the fact that $H_\alpha$ is a complex line. This complication may now be avoided in the experiments, since quantum mechanics has permitted a satisfactory theoretical interpretation of the effect of the fields on the single lines of parhelium.[†] Without detracting from the fundamental importance of the early visual observations of Garbasso, therefore, it is the present purpose to record photographs of the effect of simultaneous parallel fields on single lines so chosen as to allow very definite interpretation of the experiments.

It is clear that the experiments can be carried out most easily in the case of lines with Stark components which can be resolved without difficulty, and yet are not greatly displaced. The danger of large Stark displacements lies in the variations of the electric field, which in such cases may easily efface the magnetic resolutions. From this practical point of view the parhelium combination line 2P — 5F (near the diffuse line λ 4388) is rather satisfactory. Its mere presence is evidence of the external electric field. The perpendicular Stark component of this line which is identified by $m = \pm 2$ in the initial state increases rapidly in intensity with increasing field until in moderate fields it is a very strong line clearly separated from its neighbours, and in addition possesses the advantage of a negligible first order Stark-effect.* The initial purpose of the experiments was to split this line with a superimposed and parallel magnetic field.

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[*] 'Ann. d. Physik.,' vol. 80, p. 437 (1926).

[†] 'Roy. Soc. Proc.,' A, vol. 117, p. 137 (1927).

*Experimental Arrangements.*—The electromagnet was recently constructed at Ryerson Physical Laboratory, Chicago, and is capable of giving rather high fields. Under present working conditions, however, with holes 11 mm. in diameter drilled through the poles, and a separation of 10 mm., the field was only 2500 gauss.

Through the poles a tube of the Lo Surdo type was so placed horizontally that the exposed cathode surface came mid-way between the poles. The light from the region near the cathode was reflected from a plane mirror oriented to give a vertical virtual image. The light was passed through a Wollaston double-image prism, and focussed on the slit by a suitable photographic lens. The slit thus received two polarised images of a source in which the magnetic field was uniform, while the electric field varied from zero to the maximum value.

The light was analysed with a large prism spectrograph. The camera is a reproduction of one belonging to a spectrograph described in an earlier paper.† The new prism chamber has been made somewhat larger, however, to accommodate six 60° prisms with faces 4 inches × 2½ inches. The diameter of the circular chamber is 18 inches. The prisms rest on a heavy iron plate which is accurately flat, and the whole is enclosed in a tight case. Included in the chamber are heating units, properly controlled to maintain the temperature constant and slightly above that of the room. Six prisms were used in the present experiments. The lenses are doublets 3 inches in diameter and have a focal length of 45 inches. This spectrograph has proved to be a very satisfactory instrument for studies of the Stark-effect, and in this connection it may be of interest to compare the results obtainable with a grating mounted at this laboratory.

The stigmatic grating spectrograph has been constructed in the manner described by Meggers and Burns.‡ The concave grating, supplied by Johns Hopkins University, has a diameter of 6 inches and 21-foot radius of curvature. There are nearly 15,000 lines to the inch. In the second order the dispersion (an important factor in Stark-effect photography) is about the same as that obtainable with the full prism spectrograph at 4100 A. Upon comparing these instruments it has been a little surprising to find that the prism spectrograph gives as good resolutions, and roughly five times the speed of the grating.

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* See photograph, Plate 7, 'Roy. Soc. Proc.,' vol. 114, p. 47 (1927).

† Foster, 'J. Op. Soc. Am. & R.S.I.,' vol. 8, p. 373 (1924).

‡ 'Sci. Papers, Bur. Standards,' vol. 18, p. 185 (1922).

*Observations.*—One effect of the superimposed magnetic field is to constrict somewhat the discharge near the cathode. In consequence of this action, the maximum electric field established was in each case nearly twice that which might have been expected in the absence of the field. In a typical experiment a potential of 8000 volts was applied to a tube 2·5 mm. in diameter, the superimposed magnetic field being at the time 2700 gauss. Under these conditions a maximum electric field of 96,000 v./cm. was developed. The current through the tube was 3 mil. amps.

The expected combined effect has been found for all principal and sharp series lines which appeared on the plates (λλ 4713, 5015, 4438), and for a few of the stronger components of the new line groups which appear in the presence of electric fields. Owing to the small separations and low intensities of many of the Stark components, however, the complete analysis could not be expected in the latter case.

Fig. 1 (Plate 10) represents the perpendicular components of the parhelium group 2P — 5Q (λ 4388) in an electric field of 63,000 v./cm., and magnetic field of 1650 gauss. The plate reproduced was exposed for 30 minutes; but a clear splitting of the central Stark component was found on the first plate with an exposure of 3½ minutes. The magnitude of this symmetrical splitting is seen to be independent of the strength of the electric field. The slight shift of the central Stark component toward the red in the higher electric fields is an effect proportional to the square of the field as first observed by Takamine.

Fig. 2, Plate 10, is a photograph of the parallel (upper) as well as perpendicular components of the orthohelium group $2p - 4q$ (λ 4471) taken when fields of 60,000 v./cm. and 2250 gauss respectively were applied to the source. In very low or zero electric field the normal Zeeman effect is observed for all lines. The new combination line on the left, $2p - 4f$, like all other new lines, appears as a doublet in the "perpendicular" image. This doublet character is clearly retained with constant separation throughout the range of electric fields by the strong perpendicular component identified by $m = \pm 2$ in the initial state (arrow). The corresponding component of the original diffuse line has the same character, though it is less clearly reproducible. The remaining Stark components are known to have such small separations that definite resolutions are not obtained in the presence of a magnetic field. The doublets are, of course, absent in the parallel image.

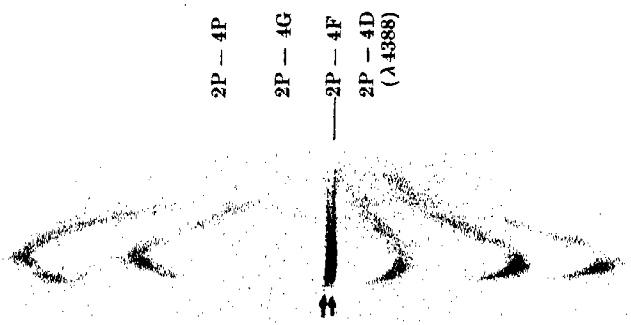

Fig. 1.

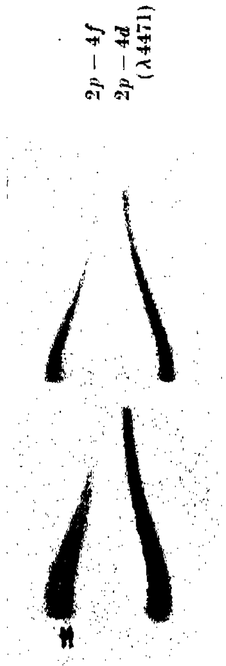

Fig. 2.

The arrows point to components which appear only in the presence of an electric field and are made double by a magnetic field.

(*Facing p.* 602.)

A point of some interest in the Stark-effect alone is the reappearance of the component G (0,1)* of the 2P — 5Q group in fields above 95,000 v./cm. It may be recalled that in an earlier paper it was shown that Stark components of this (and similar groups), which are identified by $m = 0, \pm 1$ in the initial state, must vanish or become especially weak respectively whenever the displacement is such that they theoretically coincide with the zero field position of the $p - p$ combination line of the same group. In higher fields, however, if the displacement continues to increase, the intensity (which is very closely connected with the displacement) will eventually become great enough for observation. As already pointed out, the components in question should return at just the field strength in which they have now been observed.

While no difficulty has been found in sustaining the discharge with crossed electric and magnetic fields, the photographs so far obtained have not been satisfactory.

## *Summary.*

Parallel electric and magnetic fields have been applied to a helium source, and the light analysed by a prism spectrograph of high dispersion.

The effects in parhelium and orthohelium are clearly additive in the sharp and principal series, and for the components of the diffuse lines which are resolved. The magnetic separation is independent of the magnitude of the Stark-effect.

Certain Stark components which were known to vanish in moderate fields now reappear under the action of stronger fields, as predicted in the quantum mechanical explanation of the Stark-effect for helium.

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* That is, the unresolved Stark components of 2P — 5G which are identified by $m = 0, \pm 1$ in the initial state.

# *Pressure Distribution in a Fluid due to the Axial Vibration of a Rigid Disc.*

By N. W. McLachlan, D.Sc., M.I.E.E., F.Inst.P.

(Communicated by F. E. Smith, F.R.S.—Received November 2, 1928.)

The advent of broadcasting has stimulated scientific interest in the reproduction of sound by the aid of moving diaphragms. There is a distinct change in the quality of reproduced music according as one stands in front or at the side of a loud speaker. This is due to non-uniform pressure distribution from the diaphragm at various frequencies. When the wave-length of sound is comparable with the radius of the diaphragm there is a focussing effect. This occurs at the higher audio-frequencies and upsets the tonal balance unless the listener is situated on the axial line of the diaphragm.

The purpose of the present paper is to examine analytically the pressure distribution in the space surrounding a flat rigid disc vibrating in a plane of infinite extent. The plane prevents interference of the sound waves emitted by the two sides of the disc.

### *Axial Pressure.*

Referring to fig. 1 the velocity potential due to an elemental ring moving axially under simple harmonic motion with velocity $\dot{x}$ is

$$\phi = - \dot{x}/2\pi \,.\, e^{-ikr}/r \,.\, (\text{area of ring}) = - \dot{x}e^{ikr} r^{-1} y\, dy. \tag{1}$$

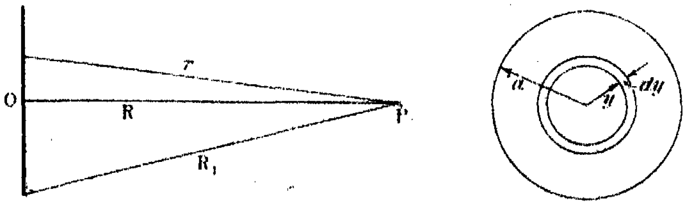

Fig. 1.

where $k = \omega/c$ and $c$ is the velocity of longitudinal waves in the fluid.

Integrating this over the surface of the disc with reference to the point P we get,

$$\phi = - \dot{x}\int_{R}^{R_1} \frac{e^{-ikr}}{r}\, r\, dr = \frac{\dot{x}}{ik}[e^{-ikR_1} - e^{-ikR}]. \tag{2}$$

The pressure at P is

$$p_a = - \rho\, d\phi/dt = - \rho\ddot{x}/ik\,[e^{-ikR_1} - e^{-ikR}] \qquad \text{from (2)}$$

$$= 2\rho\ddot{x}/k \,.\, e^{-ik/2\,(R_1+R)} \sin k/2\,(R_1 - R). \tag{3}$$

Apart from phase, the pressure at a point P on the axis of the disc is

$$p_a = 2\rho\ddot{x}k^{-1} \,.\, \sin \tfrac{1}{2}k\,(\mathrm{R}_1 - \mathrm{R}). \qquad (4)$$

Expression (4) indicates that when $\sin \frac{1}{2}k\,(\mathrm{R}_1 - \mathrm{R}) = 0$, or when $\mathrm{R}_1 - \mathrm{R} = 2\pi n/k$, the pressure vanishes, *i.e.*, a node occurs. The last expression can be written $\mathrm{R}_1 - \mathrm{R} = n\lambda$, where $\lambda$ is the wave-length and $n$ is a positive integer.

As an example, let $a = 10$ cm., $f = 4096$ cycles, then in air at N.T.P. $\lambda = 8{\cdot}25$ cm. and there is only one node which occurs $1{\cdot}93$ cm. from the disc. When $f = 8192$ cycles there are two nodes which occur at distances of $1{\cdot}93$ and 10 cm. respectively from the disc. In general, the last node—farthest from the disc—occurs when $n = 1$.

When R the distance from the disc is large compared with the radius $a$ we can write

$$\mathrm{R}_1 - \mathrm{R} = a^2/2\mathrm{R} \quad \text{and} \quad \sin \tfrac{1}{2}k\,(\mathrm{R}_1 - \mathrm{R}) = ka^2/2\mathrm{R}. \qquad (5)$$

Substituting the value from (5) in (4) we obtain the axial pressure

$$p_a = \rho\ddot{x}a^2/2\mathrm{R}. \qquad (6)$$

Thus at a point whose distance exceeds, say, five diameters, the axial pressure is proportional directly to the acceleration of the disc and inversely to the distance from the disc.

### *Pressure at Point Remote from Axis.*

From geometrical considerations of fig. 2 we have

$$r^2 = b^2 + c^2 + y^2 - 2by\cos\theta = \mathrm{R}^2 + y^2 - 2by\cos\theta.$$

Since $b = \mathrm{R}\sin\phi$ we get

$$r^2 = \mathrm{R}^2 + y^2 - 2\mathrm{R}y\sin\phi\cos\theta = \mathrm{R}^2\{1 + y^2/\mathrm{R}^2 - 2y/\mathrm{R} \,.\, \sin\phi\cos\theta\}. \qquad (7)$$

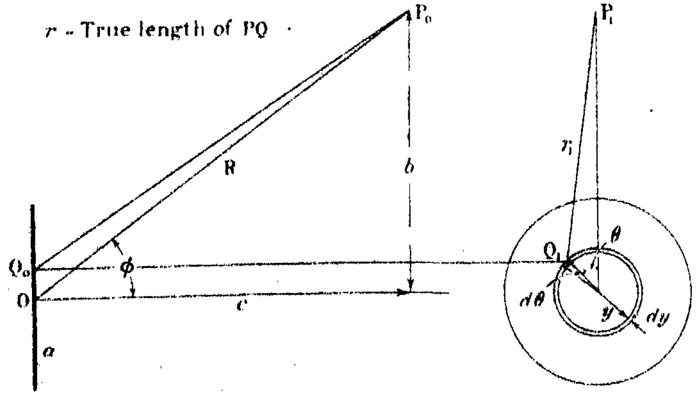

FIG. 2.

If $y/\mathrm{R}$ is small, $y^2/\mathrm{R}^2$ can be neglected in comparison with unity, although it is greater than $2y/\mathrm{R} \,.\, \sin\phi\cos\theta$ when $\phi = 0$, $\pi$ or $\theta = \frac{1}{2}\pi$, $\frac{3}{2}\pi$. Thus from (7)

$$r \doteqdot \mathrm{R}\,(1 - y/\mathrm{R} \,.\, \sin\phi\cos\theta). \tag{8}$$

The velocity potential at a point P, remote from the axis, due to an elemental area $ds$ at Q moving axially with velocity $\dot{x}$ is,

$$\phi = -\frac{\dot{x}}{2\pi}\int\frac{e^{-ikr}}{r}\,ds, \tag{9}$$

where $ds = y\,dy\,d\theta$.

Substituting the value of $r$ from (8) in (9) we have

$$\phi = -\frac{\dot{x}}{2\pi\mathrm{R}}\int_0^a\int_0^{2\pi} e^{-ik(\mathrm{R}-y\sin\phi\cos\theta)}\,y\,dy\,d\theta,$$

where R in the denominator is written in place of $\mathrm{R} - y\sin\phi\cos\theta$ since $y\sin\phi\cos\theta$ is negligible by comparison.

From above we obtain

$$\phi = -\frac{\dot{x}}{2\pi}\,.\,\frac{e^{-ik\mathrm{R}}}{\mathrm{R}}\int_0^a\int_0^{2\pi} y\,.\,e^{iky\sin\phi\cos\theta}\,dy\,d\theta. \tag{10}$$

Taking the first integral we have

$$\int_0^{2\pi} e^{iky\sin\phi\cos\theta}\,d\theta = \int_0^{2\pi}\{\cos(\psi\cos\theta) + i\sin(\psi\cos\theta)\}\,d\theta$$

where $\psi = ky\sin\phi$.

Now

$$\int_0^{2\pi}\sin(\psi\cos\theta)\,d\theta = 0,$$

and, therefore,

$$\int_0^{2\pi} e^{iky\sin\phi\cos\theta}\,d\theta = \int_0^{2\pi}\cos(\psi\cos\theta)\,d\theta = 2\pi\mathrm{J}_0(\psi) \tag{11}$$

Substituting the result from (11) in (10) we get

$$\phi = -\frac{\dot{x}e^{-ik\mathrm{R}}}{\mathrm{R}}\int_0^a \mathrm{J}_0(ky\sin\phi)\,y\,dy. \tag{12}$$

But

$$\int_0^{\psi}\psi\mathrm{J}_0(\psi)\,d\psi = \psi\mathrm{J}_1'(\psi), \tag{13}$$

and

$$\psi = ky\sin\phi \quad \text{or} \quad dy = d\psi/k \,.\, \sin\phi.$$

Substituting, we find

$$\int_0^a J_0(ky \sin \phi) \,.\, y\, dy = \frac{1}{k^2 \sin^2 \phi} \int_0^{ka \sin \phi} \psi\, J_0(\psi)\, d\psi$$

$$= ka \sin \phi / k^2 \sin^2 \phi\, [J_1(ka \sin \phi)] \qquad \text{from (13)}$$

$$= a^2 [J_1(ka \sin \phi)/ka \sin \phi]. \tag{14}$$

Hence

$$\phi = - \dot{x} a^2 e^{-ikR}/R \,.\, [J_1(ka \sin \phi)/ka \sin \phi]. \tag{15}$$

Thus the air pressure at P is given by

$$\phi = - \rho\, d\phi/dt$$

$$= \rho \ddot{x} a^2/R \,.\, e^{-ikR}[G_1], \quad \text{where} \quad G_1 = J_1(ka \sin \phi)/ka \sin \phi.$$

The scalar value of $p$ is, therefore—writing $r$ for R since they are almost equal at distances of 5 diameters or more—

$$p = \tfrac{1}{2} \rho \ddot{x} a^2 r^{-1} \,.\, 2G_1 \tag{16}$$

$$= \text{axial pressure} \times 2G_1. \tag{17}$$

The function $G_1$ is plotted against $ka \sin \phi$ in fig. 3. Starting at 0·5 it gradually falls to zero and then oscillates about this value. Interpreted in the physical sense, the fall to zero corresponds to the reduction in pressure due to interference of the radiation in the space beyond the disc. Zero value indicates zero pressure, that is the practical limit of the radiated pressure beam. Thereafter the pressure is alternately positive and negative (relatively) but of small value compared with that on the axis of the disc.

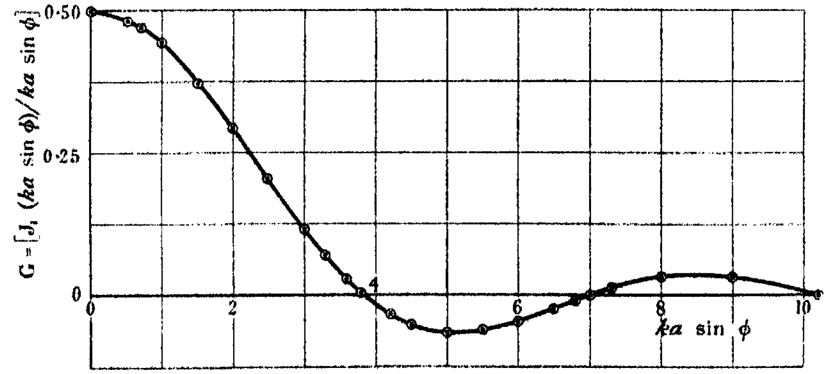

FIG. 3.

There are two interesting values of $ka \sin \phi$. When its value is 2·2 the pressure is halved, and when $3 \cdot 83$ the pressure is zero, *i.e.*, a nodal surface. Beyond the latter point there follow the negative and positive zones, these being separated by nodal surfaces.

In air at N.T.P. the angle of the first nodal surface at which $p = 0$ is given by the relationship $\phi = \sin^{-1} 2 \times 10^4/af$.

For a disc 10 cm. radius at 4096 cycles—top note on the piano—the angle $\phi$ is approximately 30°, whilst at 8192 cycles $\phi = 14 \cdot 5°$ which is quite a narrow beam. For larger discs the focussing would be more pronounced, *i.e.*, the angular width of the beam would be less.

In fig. 4 are shown polar curves of pressure distribution of discs 5 and 10 cm. in diameter at frequencies corresponding to the middle and the top of the pianoforte. The medium under consideration is air at N.T.P. In order to avoid confusion, only the main polar curves at 4096 cycles are shown. The complete diagram contains small ovals at each side of the main curves. The relative magnitude of the pressures at various angular distances can be obtained from the data given in the table below.

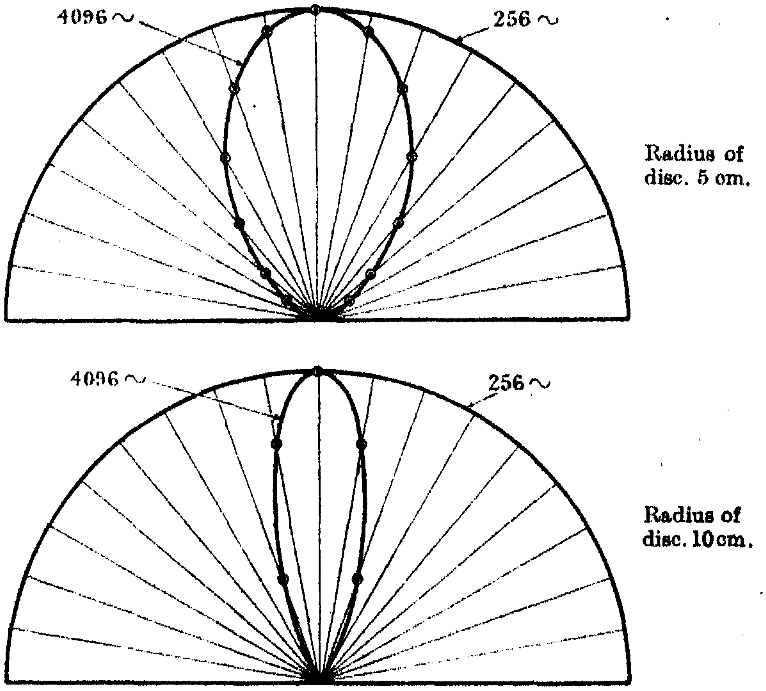

FIG. 4.

From fig. 4 it is clear that the width of the central beam decreases with increase in the frequency of vibration and also with increase in the diameter of the disc.

It may be inferred from this analysis that for uniform pressure distribution over a hemispherical surface, the disc ought to approximate to a point source. In practice this is discountenanced owing to limitations imposed by the driving agent due to the relatively large amplitudes required to radiate the lower frequencies. If a disc 1 cm. radius were driven by an annular coil in a radial magnetic field, the back e.m.f. due to the motion of the coil at frequencies below 200 ~ would cause a considerable reduction in the current and therefore in the force on the disc.

Table showing Values of $2G_1$ for various Values of $\phi$. In plotting fig. 4 the Axial Pressures at 256 ~ and 4096 ~ have been assumed equal.

| Angular distance $\phi$ degrees. | Function $2G_1$. | |
|---|---|---|
| | Disc 5 cm. radius. | Disc 10 cm. radius. |
| 0 | 1·0 | 1·0 |
| 10 | 0·94 | 0·78 |
| 20 | 0·79 | 0·35 |
| 30 | 0·6 | −0·015 |
| 40 | 0·4 | −0·13 |
| 50 | 0·22 | −0·09 |
| 60 | 0·11 | −0·024 |
| 70 | 0·04 | +0·02 |
| 80 | 0·0 | +0·045 |
| 90 | −0·015 | +0·05 |

# *The Mechanism of the Homogeneous Combination of Hydrogen and Oxygen.*

By H. W. THOMPSON and C. N. HINSHELWOOD.

(Communicated by Sir Harold Hartley, F.R.S.—Received November 21, 1928.)

According to the generally accepted belief, molecules do not, in most chemical reactions, undergo transformation until they have had imparted to them by some physical agency, such as collision with another molecule, a certain critical amount of energy. This process is commonly called "activation." Ordinarily it is governed by the energy distribution laws prevailing in a system in thermodynamic equilibrium, but in exothermic reactions a special mechanism has been shown to be possible, in which the energy set free is communicated by the molecules formed in the reaction to untransformed molecules, and immediately activates them, thereby establishing what is known as a reaction chain.

In a theoretical discussion of the matter Christiansen and Kramers* have called attention to the fact that these chains may be of two kinds. In the first kind each act of chemical transformation does not produce more than one molecule capable of continuing the chain; and since the chain may be interrupted by various circumstances, a "stationary" condition will be established when the number of chains starting in unit time is equal to the number which are terminated.

In the second kind more than one activated molecule is produced at each link of the chain, and the velocity of reaction may increase indefinitely, no stationary condition being possible.

The velocity of a chain reaction can be expressed in a general way by the formula

$$v = \mathrm{F}(c)/\{f(c, s) + \mathrm{A}(1 - \alpha)\},$$

where F(c) is a function of the concentrations of the reacting substances, to which the number of chains starting in unit time is proportional; $f(c, s)$ is another function of the concentrations, or of the surface of the vessel, governing the rate of breaking of the chains; A is a constant in reactions where only one kind of molecule is involved, but in reactions between two kinds of molecules is a function of concentration; and $\alpha$ is a fraction which measures the average number of activated molecules produced in each act of transformation.

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* 'Z. Phys. Chem.,' vol. 104, p. 451 (1923).

If $\alpha \leqq 1$ this expression, although it may become large, is always finite. Thus in the first kind of chain, a stable or "stationary" velocity, by which is to be understood one which does not increase with time, is always possible. In the second kind where $\alpha > 1$ the velocity becomes infinite at the point where

$$f(c, s) = -A(1-\alpha),$$

$\alpha$ itself may vary somewhat with concentration, and when $f(c, s)$ is small, a very small change in $\alpha$ may cause the reaction velocity to change suddenly from a finite magnitude to infinity, which means to say that a very small change in concentration may result in an abrupt transition from slow reaction to explosion. This was first pointed out by Semenov.* Chains in which a stable velocity is established probably occur in the combination of hydrogen with chlorine, in the oxidation of certain aldehydes, and in other reactions;† while Semenov has recently shown that in the oxidation of phosphorus vapour by oxygen at low pressures the velocity may become non-stationary at a certain critical pressure, below which the reaction is extremely slow, and above which it is explosive. A critical pressure of this kind is quite different from one above which explosion occurs because the reaction has become so rapid that conditions can no longer remain isothermal.

The combination of hydrogen and oxygen in the gas phase at temperatures between 500–600° C. is a chain reaction.‡ Since the velocity is very much decreased by increasing the extent of the surface of the containing vessel, and very much increased by the presence of foreign gases, it must be supposed that the principal way in which the chains are interrupted is by some deactivation process occurring at the walls, the foreign gas lengthening the chain by keeping the active molecules out of contact with the surface, rather than breaking it by depriving them of their energy. These chains are propagated with a stable velocity which increases rapidly with temperature and concentration up to the point where the normal thermal explosion takes place.

A small amount of nitrogen peroxide in the gas can, however, initiate a non-stationary process.§ At temperatures and concentrations of hydrogen and oxygen where the rate of the normal combination is negligibly small there is an upper and a lower critical concentration of nitrogen peroxide, above and below which limits the velocity of reaction is negligible, but between which there is instantaneous ignition of the hydrogen and oxygen. The transitions are abrupt, there being no intermediate region of high "stationary" velocity.

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* 'Z. Physik,' vol. 46, p. 109 (1927) and vol. 48, p. 571 (1928).

† Thon, 'Fort. Chem. Phys.,' vol. 18, p. 23 (1926); Bäckström, 'J. Amer. Chem. Soc.,' vol. 49, p. 1460 (1927).

‡ Hinshelwood and Thompson, 'Roy Soc. Proc.,' A, vol. 118, p. 170 (1928); Gibson and Hinshelwood, *ibid*, vol. 119, p. 591 (1928).

§ Gibson and Hinshelwood, 'Proc. Faraday Soc.' vol. 24, p. 559 (1928), arising from H. B. Dixon's work on ignition temperatures.

### *Chains of Non-stationary Type in Mixtures of Hydrogen and Oxygen alone.*

It has now been found that the stationary chain process occurring in the reaction between hydrogen and oxygen at higher pressures, may give place to a non-stationary one leading to explosion at lower concentrations. In the previous experiments, where hydrogen was always admitted to the reaction vessel first, and oxygen subsequently, it was observed that ignition always took place as the oxygen entered, if the pressure of hydrogen were too small: this was in keeping with the experiments of Dixon,* who found that when oxygen was admitted to an atmosphere of hydrogen by a jet, the ignition temperature decreased with the pressure.

At first we were inclined to believe that this phenomenon was only of secondary importance, and connected with the thermal conductivity of the gases, and the peculiar conditions prevailing in the region where they met, rather than with the reaction velocity in the uniform mixture which would have resulted had inflammation not occurred. The phenomenon was nevertheless investigated further, and proved to be fundamental. The first experiments were made by finding the minimum pressure of hydrogen in which oxygen would no longer ignite as it entered through a capillary tube into a silica reaction bulb of about 250 c.c. capacity at 550° C. When the pressure of hydrogen is greater than 84 mm. mercury, no inflammation takes place, but only the normal reaction, which at this pressure is rather slow. Immediate inflammation occurs at all hydrogen pressures between 84 mm. and 30–40 mm., below which limit the combination suddenly becomes very slow. If, on the other hand. hydrogen is admitted to oxygen, the upper pressure limit is 135 mm. oxygen. If the pressure of hydrogen or oxygen is less than the upper critical limit, ignition can be prevented by previously introducing an amount of argon equal to about three times the deficiency of hydrogen or oxygen.

If the hydrogen or oxygen are mixed in the desired proportion before admission to the reaction vessel at 550° C., ignition occurs as soon as the pressure in the vessel passes the lower limit: this circumstance makes it mpossible to pass the upper limit. The exact position of the lower limit was difficult to determine owing to the feebleness of the explosion at such low concentrations. These experiments prove that the ignition in the region of low pressures does not, as was originally suspected, occur only when a jet of one gas is surrounded by a complete atmosphere of the other, but must depend upon the establishment of non-stationary reaction chains in the mixture.

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* 'Mem. Proc. Manch. Lit. Phil. Soc.,' vol. 70, p. 29 (1926).

The most satisfactory method of investigating the position of the upper critical limit was found to be as follows: Hydrogen was first admitted to the reaction bulb at a pressure great enough to allow the admixture of a known amount of oxygen without inflammation. The mixture was then slowly withdrawn through the tap leading to the pump. When the total pressure had fallen to a quite sharply defined value, explosion occurred. The amount of normal reaction which occurred during withdrawal up to the instant of the explosion was quite negligible. The occurrence of the explosion was found to be determined simply by the pressure, and not by the rate of withdrawal, or the exact length of time during which the mixture had remained in the vessel; thus it is not in any way a "time-lag" phenomenon. The results obtained by this method have more quantitative significance than those described above, but are quite consistent with them.

The following facts about the upper critical pressure were ascertained:—

(*a*) At a given temperature it is slightly lowered by an increase in the ratio $H_2/O_2$ in the mixture

| Temperature. | Ratio hydrogen to oxygen. | Total pressure $H_2 + O_2$. |
|---|---|---|
| 550° C. | 0·5 | 129 |
| | 0·67 | 115 |
| | 1·0 | 97 |
| | 2·0 | 99, 99 |
| | 3·0 | 83 |

(*b*) It is somewhat lowered by the presence of argon, but not very markedly. Thus at 550° C. the critical pressure for a mixture $[2H_2 + O_2 + 2A]$ was 137 mm., *i.e.*, 55 mm. argon and 82 mm. of $[2H_2 + O_2]$; thus 55 mm. argon lower the critical pressure of the reacting gases from 99 mm. to 82 mm. Further examples will be given in the table below.

(*c*) The critical pressure at any temperature over a wide range is almost, if not quite, independent both of the nature and extent of the surface of the reaction vessel. Experiments were made in three vessels, a capillary-necked silica bulb of about 300 c.c. capacity; an identical bulb containing 17 lengths of silica tubing open at both ends and packed vertically so as to fill it completely; and a bulb of Worcester porcelain. Detailed results are given in the table below.

(*d*) The critical pressure diminishes rapidly as the temperature falls.

Table I.

(i)

| Temperature °C. | Critical pressure in mm. mercury $2H_2 + O_2$ in unpacked silica bulb. | |
|---|---|---|
| | | average |
| 570 | 134, 132, 132 | 132 |
| 560 | 113, 114 | 114 |
| 550 | 99 | 99 |
| 539 | 76, 79 | 78 |
| 530 | 61, 61 | 61 |
| 511 | 41, 42, 42 | 42 |
| 500 | 32, 33 | 33 |
| 489 | 26, 25 | 25 |
| 480 | 21, 21 | 21 |
| 460 | 10, 11, 11 | 11 |
| 440 | no explosion at all. | |

(ii)

| Temperature °C. | Critical pressure in mm. mercury $[2H_2 + O_2]$ in silica bulb packed with tubes. | |
|---|---|---|
| | | mean |
| 581 | 151, 154 | 154 |
| 560 | 107, 110, 108 | 108 |
| 546 | 85, 82, 82 | 82 |
| 530 | 63 | 63 |
| 529 | 62 | 62 |
| 507 | 36, 40, 38 | 38 |

(iii)

| Temperature °C. | Critical pressure in mm. mercury $[2H_2 + O_2]$ in porcelain bulb. | |
|---|---|---|
| | | mean |
| 569 | 127, 121 | 124 |
| 560 | 105, 101 | 103 |
| 551 | 84, 84 | 84 |
| 580 | 49, 56, 56 | 56 |
| 516 | 37, 40, 39 | 39 |
| 500 | 35, 27, 27 | 27 |
| 473 | no explosion at all. | |

Table I—(continued).

(iv)

| Temperature ° C. | Critical partial pressure of $2H_2 + O_2$ in mm. mercury. | Pressure of argon at critical point. |
|---|---|---|
| 565 | 107 | 71 |
| 563 | 95 | 63 |
| 550 | 82 | 55 |
| 548 | 80 | 53 |
| 520 | 42 | 28 |
| 506 | 28 | 19 |

The determination of the exact position of the lower limit as already mentioned is, for purely practical reasons, very difficult. The experiments which have just been recorded yield, however, a certain measure of indirect information about its position. The temperature at which ignition ceases entirely will be that at which the upper and lower pressure limits coincide. In the unpacked silica bulb this temperature was about 450° C., whence from the curve in fig. 1 the limit would appear to be approximately 8 mm.

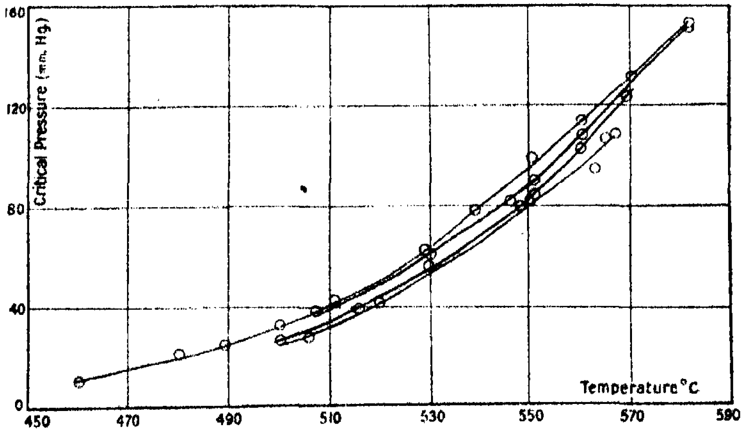


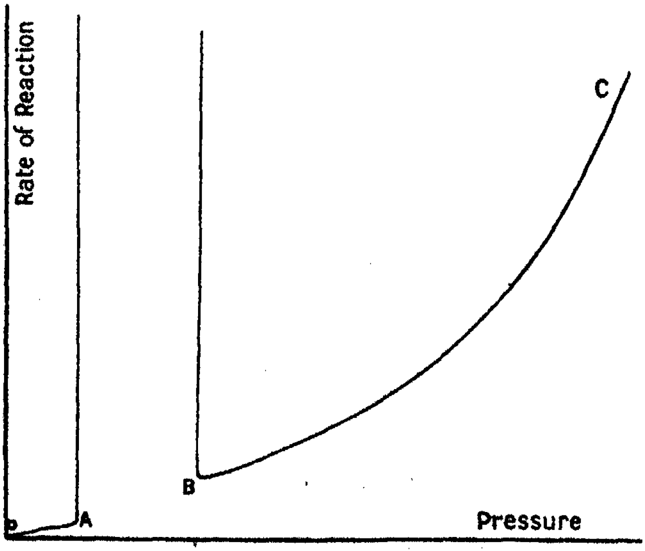
Fig. 1.

That the upper limit is independent of the surface of the reaction vessel is the more striking since the velocity of reaction when the concentrations are above this limit is much diminished by increasing the surface. To avoid any possibility of error, the truth of this fact, although fully established in the earlier experiments, was again confirmed by making measurements in the two silica bulbs referred to above. These had been specially constructed so as to be identical in every respect, except that of the tubular packing of one.

| Temperature = 555° C. | Time for 50 per cent. reaction in— | |
|---|---|---|
| | Unpacked bulb<br>volume = 301 c.c.<br>area = 256 sq. cm. | Packed bulb<br>volume = 230 c.c.<br>area = 1245 sq. cm. |
| | ′ ″ | ′ ″ |
| 400 mm. $H_2$ with 200 mm. $O_2$ | 3 14 | 40 46 |
| 200 mm. $H_2$ with 100 mm. $O_2$ | 14 0 | 250 0 |
| 200 mm. $H_2$, 100 mm. $O_2$ and 379 mm. $N_2$ | 3 53 | 180 0 |

*Theoretical Discussion.*

Combining the results of this with those of the previous investigations, it now becomes apparent that the relation between reaction velocity and pressure must be represented by a curve of the form shown in fig. 2.



Fɪɢ. 2.

The most remarkable fact about the critical limit at B, where the velocity becomes infinite, is that it terminates a region of falling reaction velocity. The dependence of reaction velocity in the region BC on the concentration of hydrogen, oxygen, foreign gases, including steam, and the surface of the reaction vessel is, in general outline at least, adequately accounted for by the working hypothesis previously advanced.*

According to this, reaction chains are initiated by a termolecular process

$$2H_2 + O_2 = 2H_2O$$

yielding active molecules of steam which hand on their energy to oxygen molecules; interruption of chains occurs principally at the walls of the vessel. In deriving the equation for the reaction velocity it was assumed that the average number of active molecules produced at each link of the chain was one, that is, the quantity "$\alpha$" mentioned in the introduction of this paper, was unity. In other words, to account for the relationships which hold in the region BC, it is necessary to suppose that chains are effectively propagated, but with a stationary velocity. The equation expressing this, is in general:

$$\text{velocity} = F(c)/\{f(c, s) + A(1 - \alpha)\}†$$

where $\alpha = 1$.

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* 'Roy. Soc. Proc.,' A, vol. 119, p. 591 (1928).

† For the purpose of this discussion the equation is best derived in the following way:—

$a'$ is the concentration of activated molecules of the reaction product, $a$ that of those of the reactant, *e.g.*, oxygen.

For stationary chains

$$\frac{da'}{dt} = 0 \quad \text{and} \quad \frac{da}{dt} = 0$$

$$\frac{da'}{dt} = f_0(c) - f_1(c)a' + \alpha f_2(c)a - f_s a' - f_e a' = 0,$$

| $f_0(c)$ | $-f_1(c)a'$ | $+\alpha f_2(c)a$ | $-f_s a'$ | $-f_e a'$ |
|---|---|---|---|---|
| Production by spontaneous reaction. | Loss by deactivation of product by reactant which takes the energy. | Production from activated molecules of reactant by reaction. | Deactivation at surface. | Deactivation in gas. |
| (1) | (2) | (3) | (4) | (5) |

$$\frac{da}{dt} = f_1(c)a' - f_2(c)a = 0.$$

| $f_1(c)a'$ | $-f_2(c)a$ |
|---|---|
| Production from activated product (process (2)). | Chemical reaction of activated reactant molecules (which produce a activated molecules of product in (3). |

$f_0(c)$, $f_1(c)$, $f_2(c)$ and $f_e$ are functions of concentration, $f_s$ of surface and concentration. Deactivation in the gas or at the surface by processes (4) and (5) is supposed to happen only to molecules of the product, not to reactant molecules; this assumption simplifies the equation, but introduces no real restriction, the breaking of the chains being thereby postponed by one link only.

Solving the equations,

$$\text{Rate of reaction} = f_2(c)a = f_0(c)f_1(c)/\{f_s + f_e + (1 - \alpha)f_1(c)\},$$

or we may write

$$\text{Rate} = F(c)/\{f(c, s) + A(1 - \alpha)\}.$$

The particular form applying to the region BC is in the notation of the previous paper

$$\text{rate} = k_1 k_3 [H_2]^3 [O_2]/k_4$$

$k_1 k_3 [H_2]^3 [O_2]$ being F(c), and $k_4$ being a function of the surface which interrupts the chains and of the inert gas concentration which tends to lengthen them. Since $2H_2 + O_2 = 2H_2O$, it is evident that, in principle, there is no reason why $\alpha$ should not exceed unity by a sufficient amount to make the whole process non-stationary. If the curve in fig. 2 is to be accounted for in this way, the expression $f(c, s) + A(1 - \alpha)$ must become zero at A and B and assume a negative value between these two points. This also is possible in principle, since the value of $f(c, s)$ is the sum of two factors, one representing deactivation by the surface, and the other by collision with molecules in the gas phase; and the first factor will decrease as the pressure increases, while the second will increase. Thus $f(c, s)$ could easily pass through a minimum at some intermediate pressure, and allow $f(c, s) + A(1 - \alpha)$ to become negative over the range where $f(c, s)$ was not large enough to balance the negative value of $A(1 - \alpha)$. In this way the general form of the whole curve can be reasonably interpreted, and with the greater plausibility since quite small relative changes in the terms of the denominator make the stationary velocity become non-stationary, and thus account for the sharp transitions at A and B.

More detailed consideration of the facts, however, leads to the conclusion that, although this explanation is probably quite correct in general outline, an additional factor is also in operation, and that the actual process by which the non-stationary chains are propagated at pressures between A and B is somewhat different from that involved in the stationary chains in the region BC.

The reason for this conclusion is as follows: Of the two deactivating factors, surface and collisions, only the second will increase with pressure; thus the upper critical limit will be reached when the deactivation or destruction of certain active molecules in the gas phase occurs rapidly enough, an inference confirmed by the fact that the upper limit is independent of the size of the reaction vessel. At pressures above the critical limit, therefore, deactivation in the gas must be playing a more important part than deactivation at the surface as far as the process operating between A and B is concerned. But it is equally certain that the process occurring between B and C is controlled principally by deactivation at the walls of the vessel.

Thus we are led to the hypothesis of two simultaneously operating mechanisms. At high pressures we may suppose that the chains are initiated by the termolecular process

$$2H_2 + O_2 = 2H_2O,$$

the evidence for which has been discussed in a previous paper; but at low pressures it is not unreasonable to assume that the termolecular process is less in evidence than a chain of bimolecular processes

$$H_2 + O_2 = H_2O_2$$
$$H_2O_2 + H_2 = 2H_2O, \quad \text{etc.}$$

For given conditions of concentration and temperature there will be a small stationary concentration of hydrogen peroxide in the gas, governed by the thermal equilibrium

$$H_2 + O_2 \rightleftharpoons H_2O_2.$$

This concentration will increase with pressure. The upper and lower pressure limits would correspond to two limiting concentrations of hydrogen peroxide, this substance appearing to play a part exactly analogous to that of nitrogen peroxide, which also induces ignition, but only when its concentration is between two sharply defined limits.*

A common explanation can now be suggested for the action of these two substances. As peroxides, they react with hydrogen, initiating reaction chains. At low pressures the stationary character of the chains can be maintained by the deactivating influence of the vessel walls; at the lower critical limit this just ceases to be possible. At higher concentrations of the peroxides their molecules will exert a mutually destructive effect, and interrupt the chains in a way analogous to that in which "antiknocks" are believed to act. When the mutually destructive action of the peroxides, whether of nitrogen peroxide upon hydrogen peroxide or hydrogen peroxide upon itself, becomes sufficiently great, we shall reach the upper critical limit, whether of $NO_2$ concentration or of hydrogen and oxygen pressure. Beyond this point the reaction by way of hydrogen peroxide becomes insignificant and the termolecular process, with its stationary chains, becomes more and more prominent as the pressure is further increased.

The advantages of this hypothesis are that it accounts for the facts about the critical limits in mixtures of hydrogen and oxygen alone, while at the same time suggesting an explanation of the remarkable influence of nitrogen peroxide; and that it makes a bimolecular process predominate at low pressures and a termolecular one at higher pressures.

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* Gibson and Hinshelwood, *loc. cit.*

If in mixtures of hydrogen and oxygen alone the initiation of the non-stationary chains depends upon the minute amount of hydrogen peroxide participating in the equilibrium

$$[H_2O_2] = K[H_2][O_2]$$

then, since the formation of hydrogen peroxide from its elements is exothermic, and $[H_2O_2]$ thus tends to decrease with increasing temperature, a greater value of the product $[H_2][O_2]$ will be necessary to provide the critical upper concentration of hydrogen peroxide as the temperature rises. This explains why the upper critical limit increases with temperature. If we may make an assumption, which admittedly can only be true as regards order of magnitude, namely, that at each temperature the critical pressure $p_c$, is reached when $[H_2O_2]$ attains some fixed value $x$, then we have, for equivalent amounts of hydrogen and oxygen,

$$x = [H_2O_2] = K[H_2][O_2] = K \cdot \tfrac{2}{3}p_c \cdot \tfrac{1}{3}p_c.$$

whence

$$p_c^2 = \text{constant}/K = \text{constant } K'$$

and

$$2d \log p_c/dT = d \log K'/dT = Q/RT^2,$$

where Q is the heat of formation of hydrogen peroxide. Plotting log $p_c$ against the reciprocal of the absolute temperature, a value of Q can be found. The curve actually obtained is accurately a straight line, the slope of which gives Q = 53,000 cals.

The heat of formation of liquid hydrogen peroxide is 47,000 cals.; the latent heat is not exactly known, but it is evident that the figure is of the order of magnitude required to account for the displacement of the limit with temperature.

It should be expressly pointed out that whether or not the details of the explanation offered prove to be fully justified, there can be no doubt that chains both of the stationary and of the non-stationary kind can be propagated in mixtures of hydrogen and oxygen. And in this connection it is perhaps not irrelevant to suggest that, if it be true that under certain circumstances the initiation of flame is more difficult in mixtures of hydrogen and oxygen that have been intensively dried than in those where small traces of water vapour are present, then it is highly probable that the peculiar action of these small quantities of water is one involving the centres of reaction from which a series of non-stationary chains are propagated.

### *Initiation of Chains in Hydrogen and Oxygen Mixtures by other Substances.*

It is now natural to enquire whether other substances can exert an effect on the combination of hydrogen and oxygen similar to that of nitrogen peroxide. A number of experiments to investigate this have been in progress for some time and the results found hitherto can be summarised as follows :—

(1) Nitrous oxide behaves in a manner generally similar to nitrogen peroxide, but is very much less effective.

(2) Hydrogen chloride causes some acceleration of the combination, but does not induce ignition.

(3) Sulphur dioxide has no observable effect on the reaction.

### *Summary.*

In previous investigations it has been shown that the homogeneous reaction between hydrogen and oxygen in the region 500–600° C. is a chain reaction, the speed of which increases rapidly with pressure. At lower pressures it is now shown that the chains become "non-stationary," and the reaction explosive, between certain definite upper and lower critical pressures. An examination of the effect of temperature, nature and size of vessel, and other factors, on the pressure limits, and a comparison of the conditions which govern the propagation of the stable reaction chains at higher pressures with those which determine the unstable chains between the two critical pressure limits, leads to the theory that at low concentrations initiation of the explosion is connected with the production of hydrogen peroxide. Molecules of the peroxide in small concentration set up chains ; at high concentrations they may exert a mutually destructive effect on one another analogous to "antiknock action." This theory also affords an explanation of the remarkable effect of traces of nitrogen peroxide on the combination of hydrogen with oxygen.

# *Adsorption at a Water Surface. Part* I.

By B. W. Currie, M.Sc., and T. Alty, D.Sc., Ph.D., F.Inst.P., Professor of Physics, University of Saskatchewan, Canada.

(Communicated by Sir Joseph Thomson, F.R.S.—Received October 30, 1928.)

It has already been shown* that the charge acquired by small air bubbles in water is due to the selective adsorption of ions by the surface molecules. The bubble surface is considered to consist of water molecules which are partly or completely orientated. These, owing to their polar nature, have a resultant electric field and therefore attract ions of one sign while repelling those of the opposite sign. In the case of water the orientation is such as to attract negative ions from the water. These ions are adsorbed on to the surface of the bubble and give it a negative charge. At the same time some of the negative ions already adsorbed will be removed by the thermal agitation of the liquid and an equilibrium state will eventually be reached in which the number striking the surface per second is equal to the number re-evaporated from it.

This adsorption of negative ions is accompanied by the capture of positive ions from the liquid. Any such positive ion striking an adsorbed negative ion may be bound to it by the electrostatic attraction so that a number of the negative ions are covered by positive ions and the charge on the bubble is due to the remaining uncovered negative ions.

In this equilibrium state the surface may be represented very diagrammatically as below.

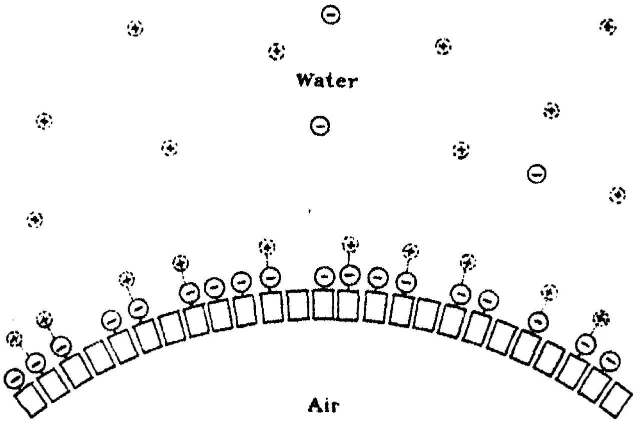

Fig. 1.—Section through Bubble Surface.

□ Orientated Surface Water Molecule. ⊖ Negative Ion. ⊕ Positive Ion.

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* 'Roy. Soc. Proc.,' A, vol. 112, p. 235 (1926).

The number of such uncovered ions will depend on the relative values of the forces binding the positive and negative ions. If the negatives are bound much more tightly than the positives a large charge will result, while if the reverse is the case the bubble will have a very small charge. Information regarding these adsorption forces may therefore be obtained from a measurement of the resultant charge when various electrolytic ions are introduced into the water.

In the previous work, the electric charge on bubbles of different diameters was determined by examining a bubble in partially air-free water. Under these conditions the bubble slowly shrinks and its charge may be determined from time to time. The chief results obtained were :—

(1) For small rates of absorption and large bubbles the charge is independent of the diameter.

(2) The greater the rate of absorption the greater the surface charge.

(3) If the rate of absorption of the bubble is appreciable the charge decreases with the diameter instead of remaining constant.

(4) In the purest water the charge is small and it was thought that in perfectly pure water it might be zero.

The increased charge with increased rate of absorption of the bubble would be expected on the theory outlined above. The air molecules passing through the surface would displace more of the loosely-bound positive ions and thus leave the bubble with a greater negative charge.

The third point tabulated above does not appear to fit in with the theory. The volume ($v$) of air passing through the surface of a bubble of radius $r$ cm. in time $dt$ is $4\pi r^2 \frac{dr}{dt} \cdot dt$ c.c. and the volume passing through 1 sq. cm. per sec. is $dr/dt$ c.c. In the experiments $dr/dt$, and therefore the number of air molecules passing through unit area per second was practically independent of $r$, so that, if the increased charge were due to collisions with these air molecules, it also would be expected to be independent of $r$. As the previous work had indicated that this was not the case special attention was paid to this point in the present experiments.

Again, if the electrification is due to the adsorption of ions, it is extremely difficult to imagine that the most active ions $H^+$ and $OH^-$, which are present even in the purest water, have no effect on the electrification. The influence of these ions has therefore been re-examined, special precautions being taken to ensure the absence of any other ion.

Returning to the first result tabulated above, it is obvious that the charge cannot continue independent of the radius indefinitely and there must be a certain critical radius beyond which the charge is no longer constant. At this critical radius the adsorbed ions will have approached each other so closely that any closer approach forces them from the surface. A measurement of the surface density at this point should, therefore, give further information about the binding forces.

It has been shown by Morrison* that the rate and manner of settling of various soils is affected by the illuminations to which they are subjected. Various types of illumination have been used on the bubble with a view to testing whether the light had any effect on the surface electrification.

The objects of this work may, therefore, be summarised as follows :—

1. Examination of the charge on bubbles having a high rate of absorption to find out if the adsorption theory definitely breaks down for such bubbles.
2. Careful measurement of the charge in pure water.
3. Examination of the charge on small bubbles so as to obtain the limit of the range in which the bubble charge is independent of the diameter.
4. Deduction from 3 of the maximum possible surface density on the bubble for different ions present in the water.
5. Test of the effect of different illuminations on the surface charge.

## *Experimental.*

The apparatus used was essentially the same as that already described.† The bubble was introduced into a cylindrical silica cell having platinum end pieces which served as electrodes. This cell was fixed between centres so that it could rotate with its axis horizontal. In order to ensure uniform and steady rotation, the cell was driven by a Rayleigh motor to which it was connected by an endless belt passing over a small pulley on one of the cell electrodes. The use of a belt containing no knot was found to be a considerable improvement as it eliminated all jerky motion of the bubble.

The Rayleigh motor used was a specially heavy one having a large moment of inertia. With a lighter type it is difficult to start the motor and any small irregularities in the tension of the belt cause the motor to stop.

Previously, the current for the motor had been rendered intermittent by passing it through the mercury break of an electrically-maintained tuning fork. With the heavy tuning forks used, a considerable current must be passed through the circuit to maintain both the tuning fork and the motor and cell. This heavy current steadily produces a layer of oxide on the surface of the mercury which sooner or later interferes with the sharp make and break of the current and stops the motor.

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* 'Roy. Soc. Proc.,' A, vol. 108, p. 280 (1925).

† 'Roy. Soc. Proc.,' A, vol. 106, p. 315 (1924).

This difficulty is conveniently overcome by using a single light steel strip instead of a tuning fork and separating the currents used to maintain the strip and the motor, that to the former passing through a platinum contact, and that to the latter through a mercury break.

The current required to drive the strip is small ($<\frac{1}{2}$ amp.) and so may be led through the platinum contact without burning it up very rapidly.

The motor current is led through a large mercury cup. The area of the mercury surface and the much smaller current passing through it greatly reduce the danger of accidentally stopping the motor.

With this method of maintenance it was usually possible to keep the motor and cell running continuously for 4 or 5 hours, so that the bubble surfaces could be examined over much longer time intervals than was previously possible.

The arrangements for measuring the conductivity of the water, the voltage applied to the cell, etc., were as described in former papers.*

On starting the motor the bubble is driven to the axis of the cell by the centrifugal force and remains there in stable equilibrium. When an electric field is applied between the ends of the cell, the bubble, if charged, will move along the axis. This motion is observed in a reading telescope and the bubble velocity deduced. Let $v$ cm./sec. be the velocity of the bubble in a field of X e.s.u./cm. Then if $\eta$ is the coefficient of viscosity of the water, $r$ the radius of the bubble and E e.s.u. the total charge on its surface, we have by Stokes Law

$$\mathrm{XE} = 6\pi\eta r v. \tag{1}$$

From this equation, the total charge E may be determined.

*Investigation of the Total Charge on the Bubble for Different Rates of Absorption.*

The previous results were first repeated. A bubble of diameter about 1·5 mm. was introduced into air-free water and its charge was measured as it decreased in size. As before, it was found that the charge steadily decreased with size, the rate of decrease being greater the greater the rate of absorption.

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* *Loc. cit.*

In a few cases when the rate of absorption was not too great there was some indication of a constant charge when the bubble was getting small. This suggested that the lack of constancy might be due to the fact that, with the high rates of absorption, the bubble disappeared before the equilibrium condition on its surface could be set up. It thus became necessary to measure the time required for equilibrium to be attained. This was done by introducing a bubble of diameter about 1·5 mm. into air-saturated water, so that its diameter remained unaltered, and measuring its charge until the latter finally became constant. In this way, it was found that the final constant charge is not attained until about 2000 seconds after introducing the bubble. This provides a very adequate explanation of the breakdown of the adsorption theory. The faster the rate of absorption of the bubble, the smaller the chance of the equilibrium charge being attained before the disappearance of the bubble.

With the new method of maintaining the motor, a further test of this point was possible. It was not practicable with the telescope used, to take measurements with bubbles of diameter greater than 2·0 mm. but, in order to give time for the surface to attain equilibrium before readings were taken, a large bubble of diameter 5 to 6 mm. was introduced into air-free water and the apparatus was left running for about an hour before any velocity measurements were made. When the size of the bubble had been reduced to 2·0 mm. in this way readings were taken in the usual manner until the bubble disappeared. This type of experiment was carried out for different rates of absorption and it was found that, *whatever this rate might be, the charge on a large bubble is independent of its diameter once surface equilibrium is attained.* Fig. 2 shows these results. It will be noticed that the higher the rate of absorption the greater the charge; a result anticipated theoretically for all rates of absorption.

The time taken for the surface to attain equilibrium is surprisingly long. In these experiments, a dilute solution of NaCl was used, the amount of salt being just sufficient to increase the conductivity of pure water to about twice its original value. If all the ions striking the surface had remained attached equilibrium would be attained in a fraction of a second. The long period actually required is a further indication of the very feeble binding forces between the adsorbed ions and the surface.

This charging period would appear to offer a direct method of comparing the binding forces of the different ions. The tighter the binding of the ions to the surface the shorter should be the time required to reach equilibrium. Consequently, the binding forces for different ions should be inversely as the corresponding times for equilibrium to be established. This relationship is examined later.

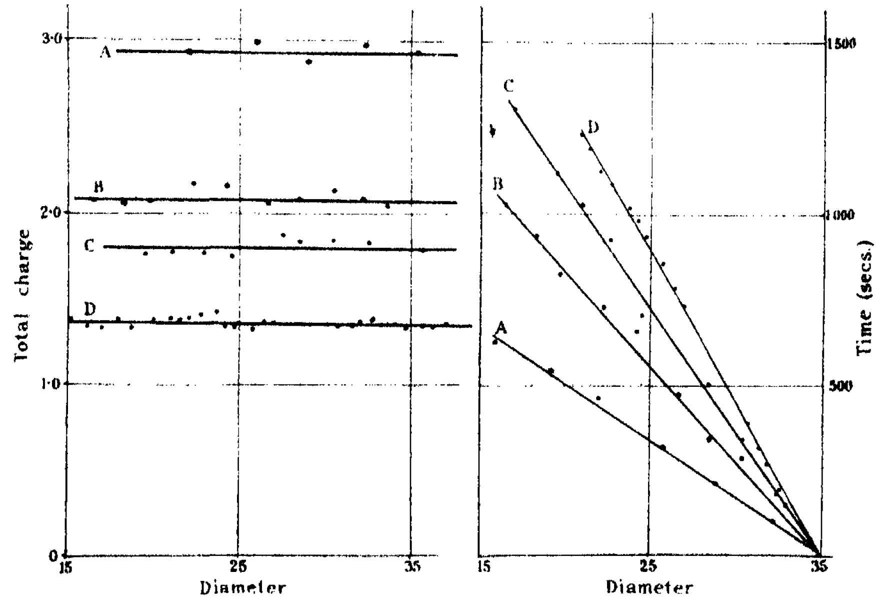

Fig. 2.

### *Examination of the Charge on Small Bubbles.*

It appears from the above that all bubbles, if they are not too small, have a charge which is independent of the radius and depends only on the rate of absorption. If a large bubble is placed in air-free water and its velocity measured until it disappears, a point is found at which the charge ceases to be constant and decreases rapidly as the radius is further decreased. In this region of decreasing charge, the bubbles are small and are not nearly so stable on the axis as are the larger bubbles, so that it is only when the apparatus is working particularly well that reliable readings can be obtained. The use of the knotless belt to drive the cell was particularly advantageous in these experiments.

The results given by the small bubbles are of two types. Usually the charge remains constant up to a certain critical radius and then falls almost instantaneously to a lower value at which it remains constant until a second critical radius is attained. A further fall in charge is then shown, so that the graph of charge-radius shows a series of steps.

A possible explanation appears to be that the adsorbed ions approach each other more and more closely as the bubble contracts, and finally part of the charge is forced off the surface by their mutual repulsions. The contraction of the surface then continues until the critical surface density for the particular radius is again attained when another fall in charge takes place. Fig. 3 shows a typical graph of charge-radius.

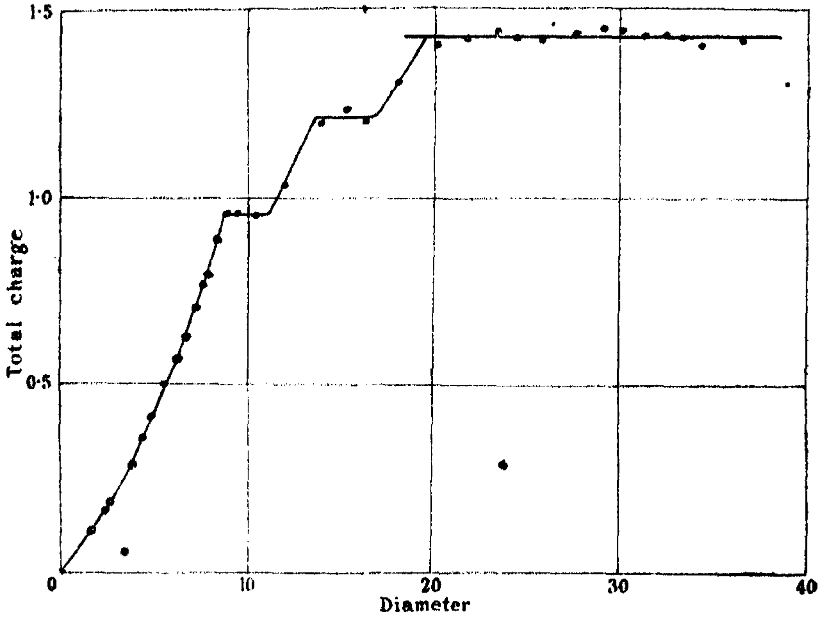

Fig. 3.—The diameter is in telescope divisions (23 divisions = 1 mm.).

The second type of result is found more rarely and so far only in very dilute NaCl solution. In this case the charge on the bubble remains constant up to a certain critical radius, depending only on the charge, after which it decreases steadily, *the surface density remaining constant.*

In these cases the graph is particularly simple, being composed of two branches, in one of which the total charge is constant and in the other the surface density is constant.

This second class of curve, giving constant surface density, is not easily obtained except in the most dilute solutions. An example showing the constant charge and constant surface density is given in Table I and fig. 4.

If T secs. = time for the bubble to cross 1 mm. then

$$v = \frac{1}{10\mathrm{T}} \text{ cm./sec.}$$

and by Stokes Law

$$E = \frac{6\pi\eta r v}{X} = \frac{6\pi\eta}{X} \cdot \frac{r}{10T} = \text{constant} \times \frac{r}{T}$$

and if $\sigma$ = surface density

$$\sigma = \text{constant}/rT.$$

Hence when the total charge is constant $r/T$ = constant, and when the surface density is constant $rT$ = constant.

In Table I the values of $r/T$ and $rT$ are given so that the range of constant charge and constant surface density can be seen. The average values of $r/T$ and $rT$ from this table are

$$r/T = 0 \cdot 955 \tag{2}$$

$$rT = 2 \cdot 79. \tag{3}$$

The curves given by (2) and (3) are plotted in fig. 4, in which the crosses

Table I.

| Diameter ($d$). | T. | $d$/T. | $d$T. |
|---|---|---|---|
| 32·75 | 17·6 | 1·86 | |
| 32·25 | 17·1 | 1·88 | |
| 31·75 | 16·9 | 1·88 | |
| 30·75 | 16·1 | 1·91 | |
| 30·25 | 15·9 | 1·91 | |
| 29·25 | 15·1 | 1·93 | |
| 29 | 15·1 | 1·93 | |
| 28·25 | 14·9 | 1·90 | |
| 27·75 | 14·1 | 1·96 | |
| 27·25 | 14·0 | 1·95 | |
| 26·25 | 14·0 | 1·88 | |
| 25·75 | 13·3 | 1·93 | |
| 25·25 | 13·2 | 1·91 | |
| 24·25 | 12·6 | 1·93 | |
| 23·75 | 12·4 | 1·91 | |
| 23 | 12·0 | 1·91 | |
| 22·25 | 11·6 | 1·93 | |
| 21·75 | 11·3 | 1·91 | |
| 21 | 11·1 | 1·90 | |
| 20·5 | 10·6 | 1·93 | |
| 19·25 | 10·0 | 1·91 | |
| 16·75 | 8·8 | 1·90 | |
| 14·25 | 7·6 | 1·88 | |
| 13·25 | 7·4 | | |
| 12·5 | 7·5 | | |
| 10·75 | 7·3 | | |
| 9·25 | 7·6 | | |
| 8·75 | 7·4 | | |
| 8 | 7·6 | | |
| 7·25 | 7·7 | | 5·58 |
| 6·5 | 8·7 | | 5·65 |
| 5·5 | 10·0 | | 5·57 |
| 4·75 | 11·7 | | 5·57 |
| 3·75 | 14·8 | | 5·54 |

(X) mark the experimental points. The two curves intersect at a diameter of 0·44 mm., the constant surface density being $5 \cdot 23 \times 10^{-3}$ e.s.u. per square centimetre.

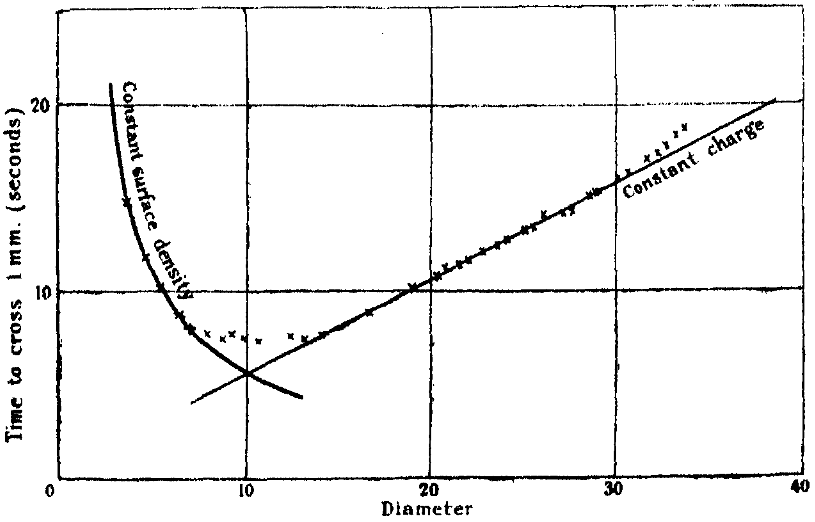

Fig. 4.

[*Added January* 14, 1929—

*Charge on the Bubble in Pure Water.*

In the earlier work (' Roy. Soc. Proc., A, vol. 106, p. 331, 1924) the water used was distilled in a glass still and had a specific resistance of $1 \cdot 6 - 2 \cdot 0 \times 10^{-6}$ ohms$^{-1}$. The experimental cell was also of soft glass and was thoroughly cleaned with chromic acid before use. It was then found that the charge on the bubble was very small.

In the present experiments, the facilities for the purification of the water were greatly increased. Distillation was carried out twice in pyrex and once in silica, and the water used was transferred to a silica cell by means of a silica pipette so that at no time was it in contact with any substance other than silica and platinum. The specific conductivity of this water was about $0 \cdot 7 \times 10^{-6}$ ohms$^{-1}$.

The original conclusion that the charge in perfectly pure water would be zero was not borne out. As the water was purified, the charge varied progressively until, after a time, further purification produced no change in the charge. This final charge was therefore taken as the charge on the bubble in pure water when only $H^+$ and $OH^-$ ions are present. In water containing other ions, the measured charge must be the resultant of that due to the ions $H^+$ and $OH^-$ and that due to the electrolytic ions introduced. This resultant charge may be either greater or less than the charge in pure water depending on the forces binding the different ions to the surface.

It is therefore evident that distillation in glass, as in the earlier work, is not sufficient. The very small charge there obtained must have been due to a minute trace of some substance dissolving from the soft glass of the experimental cell or distilling over with the water.

The results obtained when all soft glass has been eliminated are very consistent and reproducible. Fig. 5 shows a typical graph of charge-diameter.

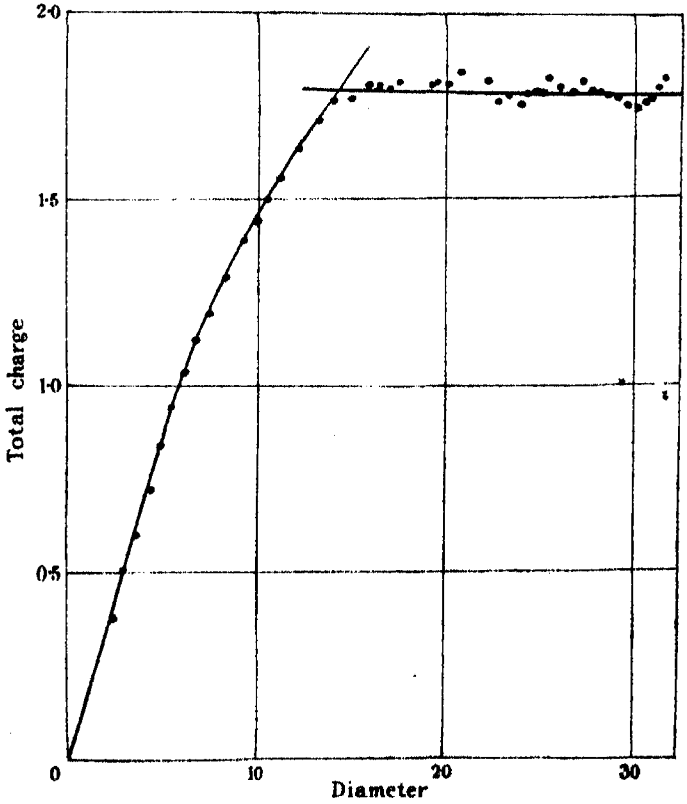

FIG. 5.

From this figure it appears that in pure water the region of constant charge extends down to a radius of 0·033 cm., this constant charge being $5 \cdot 4 \times 10^{-4}$ e.s.u.]

An interesting feature of this work in pure water is the absence of any appreciable charging period. When the bubble is introduced into the water, readings may be taken immediately without waiting for the bubble to acquire a charge. The first few readings are a little uncertain but show no steady charging. In this respect the $H^+$ and $OH^-$ ions are very different from all other ions investigated.

### *Effect of the Colour of the Light used to Illuminate the Bubble.*

It has been shown by Morrison* that when a soil solution is illuminated by a beam of light, it settles in strata, whose thickness depends on the colour of the light used. As the bubble in the present experiments is usually illuminated by red light, it was considered advisable to see if this light affected its charge.

The apparatus was arranged so that the cell could be illuminated by blue and red light alternately. The mobility was then measured several times in red light, then in blue, then in red and so on. This was continued until the bubble disappeared and all the observations were plotted on the same graph (fig. 6). It appears that all the points lie on one smooth curve, so that the effect of the different lights, if present at all, must be small.

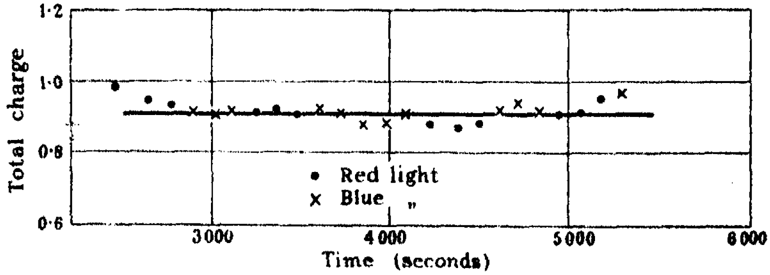

Fig. 6.

The experiment was repeated using a quartz mercury lamp instead of the blue light. No appreciable effect could be detected.

### *Summary.*

The electric charge on small air bubbles has been measured under a variety of conditions. The results indicate that :—

1. If the bubble has a diameter greater than a definite critical size, the total charge on the bubble is independent of its diameter under all conditions.
2. The greater the rate of absorption of the bubble the greater is its total charge.

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* *Loc. cit.*

3. The time required for the surface to attain its equilibrium charge has been measured and found to be about 2000 seconds in the case of dilute NaCl solution.
4. In pure water the charging period is very short (less than 200 seconds).
5. The charge on a bubble in very pure water is $5 \cdot 4 \times 10^{-4}$ e.s.u.; the critical radius in this case being $0 \cdot 033$ cm.

In Part II the critical radii and charges of a number of electrolytic ions will be examined with a view to comparing the forces binding these different ions to the surface.

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# *The Thermal Conductivity of Solid and Liquid Sulphur.*

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(Communicated by Sir Joseph Petavel, F.R.S.—Received November 25, 1928.)

By reason of the multiplicity of its solid and liquid phases, the physical and chemical properties of sulphur have been the subject of many investigations in the past. The technique of measuring thermal conductivities using a temperature drop across the specimen of only a few degrees has reached a precision which affords an additional means of exploring change-point regions. An investigation has therefore been undertaken of the thermal conductivity of solid and liquid sulphur over a range of temperature from 20° C. to 210° C., a region which embraces the transition point from rhombic ($\alpha$) to monoclinic ($\beta$) sulphur (95° C.), the "natural" melting point of monoclinic sulphur (115° C.), and the well-known change-point of liquid sulphur (160° C.) with its conspicuous alterations in physical properties (fig. 1).

In the case of solid sulphur, measurements have been made of the thermal conductivity of the rhombic and monoclinic varieties each in the form of crystalline aggregates. The influence of the previous thermal history of a sample of sulphur on the velocity of the reversible rhombic-monoclinic transformation has been demonstrated by thermal conductivity measurements. In addition, measurements have been made on the "plastic" variety of sulphur obtained by the sudden chilling of molten sulphur near its boiling point, the progressive change in thermal conductivity being followed during the slow transition at room temperature from the unstable plastic to the stable rhombic form. It has also been shown by conductivity experiments how the rapidity of this transformation is influenced by the temperature.

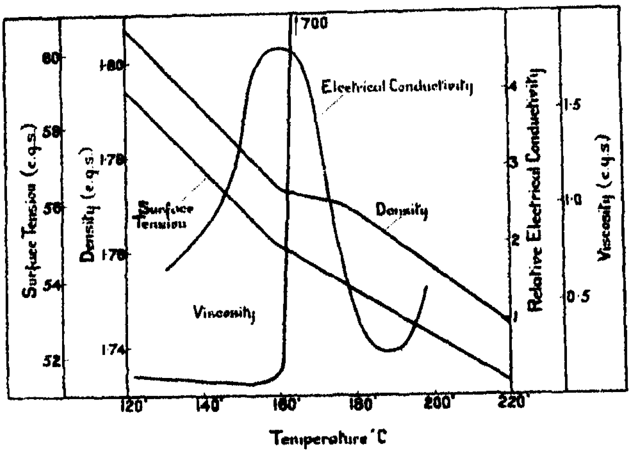

FIG. 1.—Some Physical Properties of Liquid Sulphur. Density: Kellas, 'Chem. Soc. Trans.,' vol. 113, p. 903 (1918); Surface Tension: Kellas, 'Chem. Soc. Trans.,' vol. 113, p. 903 (1918); Viscosity: Farr and Macleod, 'Roy. Soc. Proc.,' A, vol. 97, p. 80 (1920); Electrical Conductivity: Black, 'Cambridge Phil. Soc. Proc.,' vol. 22 (iii) (1924).

In the case of liquid sulphur, determinations have been made of the thermal conductivity from the melting point of monoclinic sulphur up to about 210° C.

In the light of the extensive researches of Smith and his collaborators,* and of Aten, liquid sulphur is to be regarded as a homogeneous mixture of three modifications S$\lambda$, S$\mu$ and S$\pi$, in dynamic equilibrium. The light-coloured mobile S$\lambda$ is generally regarded as the liquid form of rhombic and monoclinic sulphur, while the dark-brown viscous S$\mu$ is looked upon as the liquid form of amorphous sulphur. Of the three modifications, S$\lambda$ is present in the greatest proportion at all temperatures, declining from about 95 per cent. at 120° C. to a nearly constant figure of about 65 per cent. at 200° C. and upwards. The proportion of S$\mu$, on the other hand, is small (about 0·1 per cent.) at 120° C. and increases to a roughly constant figure of about 30 per cent. at a temperature of 200° C. and upwards. The third modification S$\pi$

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* Smith, Holmes and Hall, 'J. Amer. Chem. Soc.,' vol. 27, p. 797 (1905) and 'Z. Phys. Chem.,' vol. 52, p. 602 (1905); Smith and Holmes, 'Z. Phys. Chem.,' vol. 42, p. 469 (1903), and vol. 54, p. 257 (1906); Smith and Carson, 'Z. Phys. Chem.,' vol. 57, p. 685 (1907), vol. 61, p. 200 (1907), and vol. 77, p. 661 (1911); Smith and Brownlee, 'Z. Phys. Chem.,' vol. 61, p. 209 (1907); Aten, 'Z. Phys. Chem.,' vol. 81, p. 257 (1912), vol. 83, p. 442 (1913), vol. 86, p. 1 (1913), and vol. 88, p. 321 (1914).

is present in small and nearly constant proportion, of the order of 5 per cent., at all temperatures up to about 200° C. Equilibrium in the liquid state establishes itself relatively slowly, and it is on this account that sulphur rapidly cooled from near its boiling point retains a high percentage of S$\mu$ and forms a plastic mass which may be regarded as undercooled liquid sulphur.

Little work appears to have been done in the past on the thermal conductivity of rhombic or plastic sulphur; and no mention has been found in the literature of any determinations in the cases of the monoclinic or the liquid phases. The results of Lees, Hecht and Eucken* are summarised in the following table:—

Table I.

| Observer. | State. | Temperature, °C. | Thermal conductivity c.g.s. units. |
|---|---|---|---|
| Lees, 1892 | ? | 14 | 0·000455 |
| Hecht, 1904 | Rhombic aggregate | 20 to 100 | 0·00063 |
| Eucken, 1911 | ,, | −190 | 0·001522 |
| ,, | ,, | 0 | 0·000700 |
| ,, | "Mainly plastic" | −190 | 0·000387 |
| ,, | ,, | 0 | 0·000470 |

The sulphur used in the present investigation was the pure crystalline variety as obtainable commercially. For the determinations in the liquid state, the sulphur was first boiled in order to free it as much as possible from dissolved gases which are apt to appear as bubbles during test and vitiate the results.

### *Apparatus.*

The thermal conductivities were determined by a "plate" method similar to that employed by the present authors† for the conductivity of liquids. The main features of this are that a thin horizontal layer of the material is sandwiched between a hot and a cold metal block between which a small difference of temperature is maintained, the hot block being uppermost. The arrangement reduces convection to a minimum when a liquid is being tested. It was, of course, essential that the conductivity measured should be associated with a small temperature difference across the specimen when regions including transition points were to be investigated. The hot block was heated electrically, heat loss in the upward direction being prevented by a guard plate, while for side losses a correction was determined and applied. The system was completely enclosed in a thermostatically controlled oven, so that the mean temperature could be varied irrespective of the temperature-drop across the specimen.

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* Lees, 'Phil. Trans.,' A, vol. 183, p. 481 (1892); Hecht, 'Ann. Physik,' vol. 14, p. 1008 (1904); Eucken, 'Ann. Physik,' vol. 34, p. 185 (1911).

† 'Roy. Soc. Proc.,' A, vol. 117, p. 459 (1928).

The apparatus is shown diagrammatically in fig. 2, many of the details of which agree with those already described in the paper mentioned above. Aluminium was chosen for the material of the blocks, as it is a good thermal conductor which is unattacked by molten sulphur. The area of the test layer was about 20 sq. cms. Temperature measurements were afforded by aluminium-constantan thermocouples, the accuracy being not less than 1/10° at temperatures up to 100° C. and not less than 1/5° at higher temperatures. The measurement of the temperature-drop across the test specimen, which was usually from 3 to 5° C., was probably accurate to within 0·02° C. An accuracy of at least 1 per cent. was aimed at in the conductivity values.

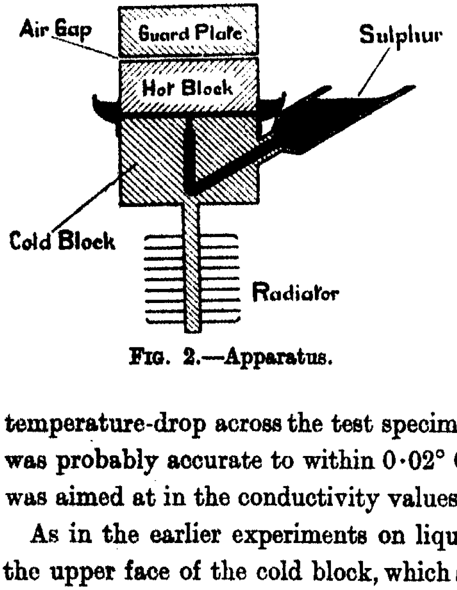

Fig. 2.—Apparatus.

As in the earlier experiments on liquids, a "gallery" was mounted round the upper face of the cold block, which served to retain the molten sulphur in position and provided a reservoir to draw on when the test layer was contracting on cooling. To facilitate the introduction of the molten sulphur and to reduce the risk of entrapped air bubbles, a side tube was provided (as shown in fig. 2) which communicated with a small central hole in the cold face.

In preparing the apparatus for tests on liquid sulphur, three silica distance pieces were placed on the surface of the cold block and the hot block was lowered into position and aligned by means of three centering screws. The oven containing the apparatus was then raised to about 150° C. and a suitable amount of liquid sulphur at about the same temperature was rapidly poured into the side tube until the gallery was full. The gallery was then covered with a mica ring, and the apparatus lagged with asbestos wool. With practice it was found possible to fill the apparatus and complete the lagging without the temperature of the test layer falling below 120° C.

For the measurements on solid sulphur, both crystalline and plastic, it was necessary to employ glycerine films[*] between the test layer and the surfaces of the hot and cold blocks. Otherwise, owing to the small thickness of specimen employed, the temperature-drop over the air films would have been of the same order as that over the specimen. In assembling the apparatus for the tests on solid sulphur, the hot block was removed, the test specimen was placed on the cold surface, and sufficient glycerine was poured into the gallery to cover the test layer completely, care being taken that no air bubbles adhered to the surface of the specimen. The hot block, slightly tilted, was carefully lowered into position and centered, the specimen being manœuvred to align exactly with the blocks, after which the excess glycerine was removed. It was found necessary to apply a load (about 16 lbs.) to the specimen to ensure uniformity of results.

The oven containing the apparatus was electrically heated and a fan was provided to circulate the air, uniformity of temperature around the apparatus being obtained by suitably placed baffles. The oven could be controlled at any desired temperature from room temperature up to about 200° C.

### *Corrections Applied to Experimental Data.*

(*a*) *Corrections for Heat Losses.*—The corrections for the lateral loss of heat and, in the case of liquid sulphur, for the heat transferred via the excess liquid in the gallery, were measured in the same way as in the earlier investigation. The correction for the heat lost by evaporation of the liquid sulphur was found to be negligible at all temperatures employed, and the calculated correction for the heat transmitted through the silica distance pieces was less than 2 per cent.

(*b*) *Temperature-drop in Glycerine Films.*—To obtain the correction for the temperature-drop across the glycerine films in the case of solid sulphur, a series of experiments was carried out in which a disc of copper replaced the test layer of sulphur, assembly being effected under glycerine in the usual way. The temperature-drop across the two glycerine films was found to be directly proportional to the power transmitted (as would be expected) and, for a given power, decreased with a rise in the mean temperature. This agrees with the known positive temperature coefficient of thermal conductivity of glycerine. The temperature-drop across the two films for a constant power transmission was found to be a linear function of the mean temperature.

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[*] In this connection, see Kaye and Higgins, 'Roy. Soc. Proc.,' A, vol. 113, p. 335 (1926); and Kaye and Roberts, Roy. Soc. Proc.,' A, vol. 104, p. 98 (1923).

Numerically the temperature-drop across the two films amounted to between 3 per cent. and 5 per cent. of the temperature-drop across the test specimen of sulphur.

### *The Thermal Conductivity of Liquid Sulphur.*

In the case of the experiments on liquid sulphur the thickness of the test layer was 0·34 mm. The earlier investigations on the thermal conductivity of liquids carried out in a similar apparatus had shown that concordant results were obtainable with liquid layers up to 0·5 mm. thick.

The results are shown graphically in fig. 3, the sequence of the observations being indicated by the numbers near the plotted points. Over the range 120° to 210° C. some 30 determinations were made representing results from three separate fillings of the apparatus. Following this, readings were taken in the region below 120° C., the temperature being gradually reduced until at about 110° C. the freezing of the test layer was indicated by a discontinuity in the readings. This temperature is somewhat lower than the "natural" melting point 115° C. and would appear to afford evidence of slight supercooling, a phenomenon to which liquid sulphur is prone.

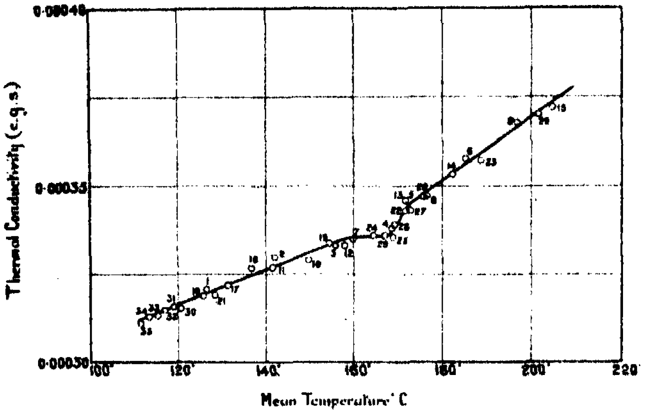

Fig. 3.—Thermal Conductivity of Liquid Sulphur.

The deviation from the mean line drawn in fig. 3 does not exceed ½ per cent. for the majority of the points, while in no case does the divergence amount to 1 per cent. The conductivity increases uniformly between 112° and 160° C. at the rate of 0·00000049 c.g.s. units per 1° C. Between 160° and 170° C. a small but definite discontinuity occurs, which is no doubt somewhat masked by the necessity of employing an appreciable, if small, temperature difference across the specimen. Despite this, the line clearly shows a flattening at about

160° C. followed at about 170° C. by a sharp rise. Thereafter a linear relationship is restored, with a somewhat higher rate of increase, viz., 0·00000088 c.g.s. units per 1° C. as compared with 0·00000049 below 160° C.

It may be noted that these discontinuities are similar in type to those observed by Kellas in determinations of the density (see fig. 1).

Table II gives values for the thermal conductivity read off from the mean line through the experimental points of fig. 3.

Table II.—Thermal Conductivity of Liquid Sulphur.

| Mean temperature, ° C. | Thermal conductivity, c.g.s. units. |
|---|---|
| 115 (M.P.) | 0·000314 |
| 120 | 0·000316 |
| 130 | 0·000321 |
| 140 | 0·000326 |
| 150 | 0·000331 |
| 160 } change-point region | 0·000336 |
| 165 | 0·000336 |
| 170 | 0·000340 |
| 180 | 0·000351 |
| 190 | 0·000360 |
| 200 | 0·000369 |
| 210 | 0·000378 |

## *The Thermal Conductivity of Solid Sulphur.*

*Preliminary Relative Measurements.*—Some preliminary experiments were conducted on a test layer of sulphur which had solidified *in situ* from the liquid state. Readings were taken as the temperature was gradually lowered, starting at the solidifying point. As sulphur contracts on solidification there was some uncertainty as to the degree of thermal contact at the surfaces of the test layer, and so the values of the conductivity obtained are subject to error. The measurements have, however, sufficient relative accuracy to display the order of the change in thermal conductivity in passing from the monoclinic to the rhombic state, as well as the time factor associated with the transformation.

The results are shown somewhat diagrammatically in fig. 4, the reference numbers against some of the observation points indicating the number of days since solidification occurred. The line AB refers to the gradual drop in temperature from the solidifying point to nearly room temperature (20° C.) spread over a period of 6 days; as will be seen, the conductivity remained approximately constant throughout. At this stage (the temperature being kept constant) a pronounced rise in the conductivity set in, as indicated by BC, the increase amounting to 50 per cent. before the value steadied up at C.

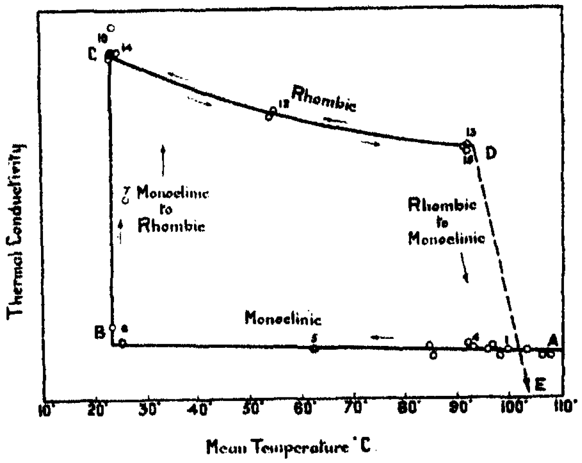

FIG. 4.—*Rhombic-Monoclinic Transformation.*

The path BC occupied about three days. The position remained unchanged at C for two days, after which the temperature was gradually raised to 90° C. (over a period of two days), the conductivity as a result moving along the line CD to D. The line CD was found to be reproducible as the temperature was altered backwards and forwards between 20° and 90° C. The temperature was now raised to about 105° C. when the conductivity at once fell (DE) to a value much below the initial line AB.

It is evident that the line AB represents the monoclinic phase resulting from solidification of the molten sulphur. BC displays the progressive transition to rhombic sulphur—the stable form below the change point at 95° C.—while CD refers to the rhombic phase. The abnormally low reading obtained on raising the temperature above 95° C. is attributable not only to the lower conductivity of the resulting monoclinic sulphur, but also (as subsequent examination showed) to fracture of the specimen due to the sudden expansion accompanying the transition, under the restrictive effect of the surrounding ring of solid sulphur in the gallery.

The sulphur used in the above experiment had solidified from liquid sulphur which had previously been raised to the boiling point, and so had been taken through the change point at 160° C. A similar experiment was then carried out with sulphur which had solidified from liquid sulphur that had not been heated above 160° C. As before, readings were taken with a gradual decrease of temperature, but now the change to rhombic sulphur began after only a few hours when the temperature had fallen to about 90° C., the transition being completed very quickly.

It thus appeared from these preliminary experiments that the change in thermal conductivity associated with the monoclinic-rhombic transition point was of an easily measurable order. Furthermore, the experiments, as far as they go, indicated that the previous thermal history of a sample of sulphur was capable of affecting the rapidity of the transformation, which is much slower when the sulphur has been previously heated to the boiling point than when its temperature has not exceeded 160° C.

*Absolute Measurements.*—Experiments were then undertaken to measure the thermal conductivity of solid sulphur more definitely. Layers about 0·6 mm. thick were used with glycerine films between the specimen and the test surfaces. The specimens were prepared by pouring over a surface plate heated to about 130° C. a pool of liquid sulphur which had not been heated above 160° C. A second surface plate also at 130° C. was lowered on to the first until it rested on four distance pieces of the desired thickness. The plates were allowed to cool slowly to 50° or 60° C. when they were slid apart and the sulphur layer removed. This operation was facilitated by previously smearing the faces of the surface plates with a trace of castor oil. Suitable test specimens were readily cut from the sulphur plates, which at first were mainly monoclinic but rapidly become rhombic. A specimen prepared in this manner showed variations in thickness of not more than 2 per cent.

*Rhombic and Monoclinic Sulphur.*—Measurements were confined in the first instance to a range of temperature from 20° to 90° C. and the results for the rhombic variety were found to lie on a reproducible smooth curve as the temperature was raised or lowered, the conductivity ranging from about 0·00065 at 20° C. to about 0·00055 at 90° C. The results are shown graphically in fig. 5, the sequence of the observations being indicated. On increasing the temperature to about 105° C. the conductivity fell abruptly by some 30 per cent. to about 0·0004 due to the transformation to the monoclinic state. The transformation was so rapid that it was not possible to obtain points of intermediate conductivity. The values for both the rhombic and monoclinic states were reproducible after repeated passages backwards and forwards through the transition point at 95° C.

These experiments were repeated with other specimens of sulphur. It was found that, while the values for the rhombic state were in close agreement for all the specimens, there was some divergence, amounting to about 6 per cent., between the values for the monoclinic state. This may possibly be due in part to the more pronounced asymmetry of the monoclinic crystals and possibly also to a varying selectiveness of orientation due to the expansion under pressure.

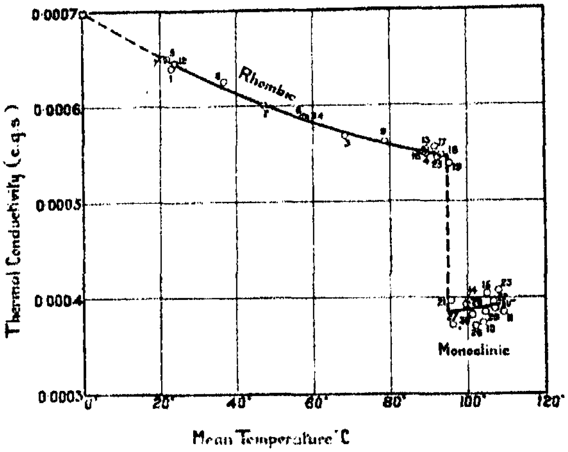

FIG. 5.—Thermal Conductivity of Solid Sulphur.

The range of temperature over which the monoclinic state exists is insufficient to reveal with certainty the temperature variation of the conductivity, though there is perhaps a slight rise with temperature. It is, however, apparent from the figures given above for liquid sulphur that there is a fall in the conductivity of about 20 per cent. at the melting point.

It may be added that the curve drawn through the experimental points in the rhombic region agrees well, if extrapolated, with Eucken's value 0·00070 at 0° C.

The results for solid sulphur are summarised in Table III.

Table III.—Thermal Conductivity of Solid Sulphur.

| State. | Mean temperature, ° C. | Thermal conductivity, c.g.s. units. |
|---|---|---|
| Rhombic aggregate.................... | 20 | 0·000652 |
| ,, .................... | 40 | 0·000613 |
| ,, .................... | 60 | 0·000581 |
| ,, .................... | 80 | 0·000558 |
| ,, .................... | 95 (change point) | 0·000547 |
| Monoclinic aggregate ................ | 100 | 0·00037–0·00040 |

*The Transformation from Plastic to Crystalline Sulphur.*

When molten sulphur is suddenly cooled from a temperature near its boiling point plastic sulphur is obtained. This hardens in the course of a few hours due to the progressive formation of rhombic sulphur, though apparently complete transformation at room temperature may take several years. Experiments were undertaken to study the return to stability in the light of conductivity measurements.

In the preparation of the specimens freshly boiled sulphur was poured over a cold surface plate, a second surface plate being immediately placed on top of the pool of sulphur. Considerable pressure was then applied until the plastic sulphur was squeezed out to the thickness of the distance pieces placed between the surfaces. It was found convenient, in view of the adhesive nature of the plastic sulphur, to coat the surface plates with a layer of tin-foil smeared with castor oil. It was then a simple matter to slide the surface plates apart, leaving the layer of sulphur coated with tin-foil. It was not usually possible to remove the tin-foil until at least 12 hours after the formation of the plastic layer; the material was however mainly plastic even after this period.

A suitable test specimen was cut from the layer and a series of measurements extending over several days was made at room temperature (about 20° C.). The results are plotted in fig. 6 where it will be seen that the conductivity at first increased rapidly and later more and more slowly. After about 8 days it had reached a value a little above 0·00060 c.g.s. units. This is not far from the value of 0·00065 at 20° C. recorded in fig. 5 for rhombic sulphur. In fig. 6 time is reckoned from the time of formation of the layer. It will be noted

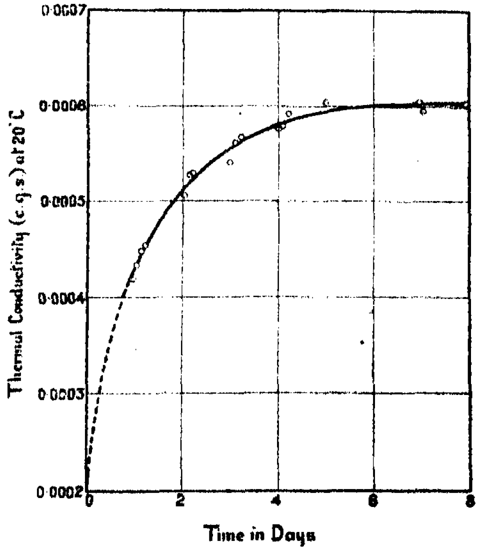

**Fig. 6.**—Transformation from Plastic to Rhombic Sulphur.

that a day had elapsed before the first measurement was taken, and an appreciable proportion of the plastic sulphur had no doubt already undergone transformation to rhombic. Extrapolating the curve backwards would indicate that the conductivity of freshly prepared plastic sulphur is relatively very low—of the order of 0·0002. It may perhaps be mentioned that such a value would lie on the curve of conductivity of liquid sulphur above 160°, when extrapolated back to room temperature.

It was desired to ascertain if the rate of transformation of the residual proportion of plastic sulphur in the specimen in question could be stimulated by a rise of temperature, and so the apparatus was raised to about 90° C. (*i.e.* just below the rhombic-monoclinic change point) for 5 hours. On cooling down to room temperature the conductivity of the specimen was now found to have increased to about 0·00073. The influence of temperature on the rate of transformation is evidently marked.

It will be noted, however, that a rise of temperature resulted not only in bringing the conductivity of the specimen up to the accepted rhombic value, but considerably beyond it. That this unexpectedly high conductivity was truly characteristic of the new structure of the specimen was shown by varying the temperature backwards and forwards over a range of from 20° to 90° C. spread over a period of five days. The curve AB in fig. 7 represents the values, which range from 0·00073 at 20° C. to 0·00059 at 90° C. and were reproducible whether the temperature was raised or lowered.

The temperature of the specimen was now raised above the change point at 95° C., with the result that the subsequent conductivity figures between 20° and 110° C. assumed the values characteristic of rhombic and monoclinic sulphur shown by curves CD and EF in fig. 7.

A similar series of experiments was then carried out on an entirely fresh sample of plastic sulphur with precisely similar results, except that the anomalously high conductivities obtained after the first heating to 90° C. were even more pronounced, the new values (curve A′B′, fig. 7) being about 0·00079 at 20° C. and 0·00067 at 90° C.

As regards the explanation of these abnormally high conductivity values, it may be that the very considerable pressure applied during the production of the plastic sulphur favours the selective orientation of a proportion of the growing rhombic crystals, in a way analogous to that produced by the cold working of metals. If a sufficient number of the rhombic crystals formed then or later conform to such selective orientation, this might well account for the abnormally high conductivity, the magnitude depending on the proportion of crystals so

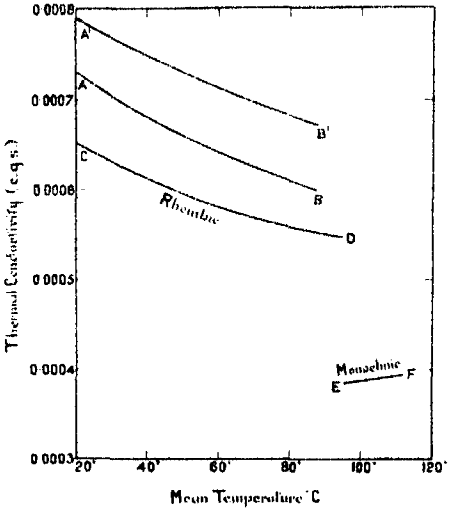

FIG. 7.—Transformation from Plastic to Crystalline Sulphur.

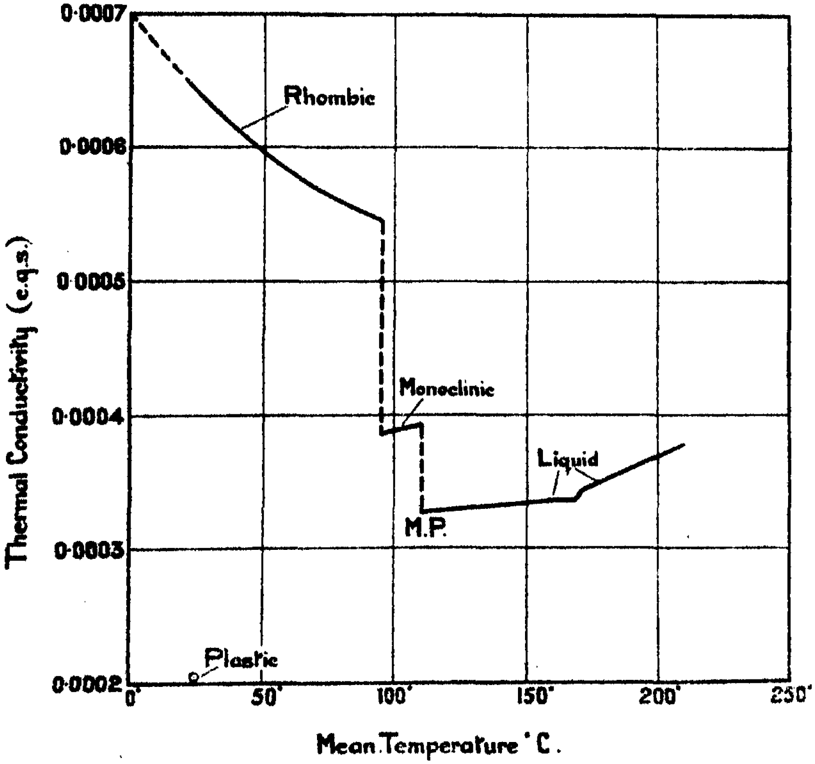

FIG. 8.—Thermal Conductivity of Sulphur.

oriented. Raising the temperature above the change point at 95° C. would destroy the orientation and result in normal rhombic and monoclinic values characteristic of a random arrangement. It will be noted for what it is worth that the temperature coefficients of the conductivity (as indicated by the slopes) for the three curves AB, A′B′ and CD are approximately the same. It was hoped to test the above explanation by the aid of X-ray spectroscopic examination, but unfortunately the results were inconclusive. Experiments on single rhombic crystals would be of interest in this connection if the experimental difficulties could be overcome.

Fig. 8 shows the complete range of variations in the thermal conductivity of sulphur as determined in the present investigation.

## *Summary.*

The thermal conductivity of sulphur has been determined over a range of temperature of from 20° C. to 210° C. by means of a "plate" method using a small temperature-drop across the specimen. The temperature range includes the transition point from rhombic to monoclinic sulphur (95° C.), the "natural" melting point of monoclinic sulphur (115° C.) and the change point of liquid sulphur (160° C.). Some observations have also been made on the "plastic" modification. In addition, the experiments show the effect of the previous thermal history on the rates of the several transformations.

The following table summarises the results :—

| State. | Mean temperature, ° C. | Thermal conductivity, c.g.s. units. |
|---|---|---|
| Rhombic aggregate | 20 | $0{\cdot}00065_2$ |
| ,, | 40 | $0{\cdot}00061_8$ |
| ,, | 60 | $0{\cdot}00058_1$ |
| ,, | 80 | $0{\cdot}00055_6$ |
| ,, | 95 (change point) | $0{\cdot}00054_7$ |
| Monoclinic aggregate | 100 | 0·00037–0·00040 |
| Liquid | 115 (M.P.) | $0{\cdot}00031_4$ |
| ,, | 120 | $0{\cdot}00031_6$ |
| ,, | 140 | $0{\cdot}00032_6$ |
| ,, | 160 } change point region | $0{\cdot}00033_6$ |
| ,, | 165 | $0{\cdot}00033_4$ |
| ,, | 170 | $0{\cdot}00034_0$ |
| ,, | 190 | $0{\cdot}00036_0$ |
| ,, | 210 | $0{\cdot}00037_8$ |
| Plastic | 20 | 0·0002 ? |

We are very glad again to acknowledge the experimental skill and pertinacity of Mr. D. E. A. Jones, of the Observer staff of the Laboratory.

# *The Absorption of Penetrating Radiation.*

By L. H. GRAY, B.A., Trinity College, Cambridge.

(Communicated by Sir E. Rutherford, P.R.S.—Received December 21, 1928.)

## § 1. *Introduction.*

A great many careful experiments in different parts of the world have established the widespread existence of a radiation which appears to be travelling downwards through the earth's atmosphere, and produces one or two ions per cubic centimetre per second in air at the surface of the earth. The nature and origin of the radiation is still uncertain, but since it is able to produce a measurable ionisation after passing through 50 metres of water it is referred to as "penetrating radiation." It has been maintained that there is nothing inconsistent with experiment in the view that penetrating radiation is in fact a beam of $\beta$-particles of great energy, and C. T. R. Wilson has pointed out that the enormous electrical fields accompanying thunderstorms would be expected to give rise to particles having energy perhaps as great as $10^9$ volts. On the other hand, the hypothesis that the new radiation is an ultra-$\gamma$-radiation has been widely adopted, and interesting numerical relations concerning the wave-lengths present in the beam, as deduced from the absorption curve of the radiation, have recently been revealed. In this paper the significance of an experimental absorption curve is investigated, more particularly with the object of arriving at a valid method of inferring from it the spectral distribution of the primary radiation.

## § 2. *The Scattering Formulæ.*

We can distinguish two processes which lead to a reduction in intensity of a beam of $\gamma$-rays in passing through matter, namely, photo-electric absorption, and the Compton scattering process which gives rise to a deflected quantum and a recoil electron. When the absorbing medium is lead and the source of $\gamma$-radiation is radium C, these two processes are of about equal importance. The former, however, varying roughly as the cube of the wave-length, decreases very much more rapidly than the latter as the hardness of the beam increases and may be assumed to be negligible for the radiation under consideration, which is at least twenty times as penetrating as the radium C $\gamma$-rays. We do not know that these are the only ways in which $\gamma$-ray energy may be absorbed. Indeed, absorption coefficients determined experimentally are in general more than 20 per cent. greater than estimates deduced with the aid of the Compton formulæ from independent evidence as to the spectral distribution of the radiation. It does not appear likely, however, that a new absorbing mechanism is indicated, but rather that the Compton formulæ are an inadequate description of the scattering process; for the interaction of radiation and free electrons has quite recently been investigated anew on the basis of a completely relativistic wave mechanic, developed from the relativity quantum mechanics of Dirac, by Klein and Nishina,* who arrive at formulæ which approach asymptotically to those of Dirac for long wave-lengths, but which differ from them already by 40 per cent. for radium C γ-rays. The old and the new formulæ diverge as the wave-length of the radiation becomes shorter, so that from the standpoint of this paper it is of the greatest importance to discriminate, if possible, between them. The points of contact of theory and experiment are discussed in § 7 and conclusions are reached which are definitely favourable to the new formulæ. All numerical computations have therefore been made in duplicate and the results to which the two sets of formulæ lead are contrasted.

The energy relations for a single scattering process merely express the conservation of energy and momentum during the interaction.

They are conveniently written

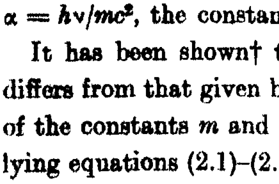

Fig. 1.

$$\tan\phi = \cot\tfrac{1}{2}\theta/(1+\alpha), \tag{2.1}$$

$$E_\beta = h\nu_0\, 2\alpha \sin^2\tfrac{1}{2}\theta/(1+2\alpha\sin^2\tfrac{1}{2}\theta), \tag{2.2}$$

$$h\nu_1 = h\nu_0/(1+2\alpha\sin^2\tfrac{1}{2}\theta), \tag{2.3}$$

$$\lambda_1 - \lambda_0 = (1-\cos\theta)\, h/mc, \tag{2.4}$$

where $E_\beta$ is the energy of the recoil electron and $\alpha = h\nu/mc^2$, the constants having their usual significance.

It has been shown† that for X-rays the observed change in wave-length differs from that given by (2.4) by less than the uncertainty in our knowledge of the constants $m$ and $h$. It appears therefore that the assumptions underlying equations (2.1)–(2.4) are valid for quanta of moderate energy, and there is no reason for supposing that energy and momentum cease to be conserved in collisions between electrons and quanta of much greater energy.

In order to calculate the frequency of occurrence of a scattering process in which the quantum is deflected through an angle lying between $\theta$ and $\theta + d\theta$

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* 'Nature,' vol. 122, p. 398 (1928).

† Sharp, 'Phys. Rev.,' vol. 26, p. 691 (1925).

it is necessary to make detailed assumptions as to the mechanism of the collision, and it is at this point that the various theories diverge. Semi-empirical formulæ have been proposed by Compton, Breit, Jauncey and others, and a treatment of the problem on the basis of the restricted relativity wave mechanics has been given by Dirac.* Since, for penetrating radiation, the absorption coefficients derived from these formulæ only differ among themselves by about 30 per cent., those of Compton, being mathematically the simplest, have been employed in these calculations. As already mentioned, calculations have also been made on the basis of the new Klein-Nishina formulæ.

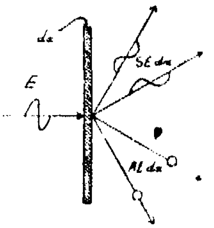

FIG. 2.

In order to avoid confusion of suffixes, the customary notation has been abandoned in favour of that exhibited in fig. 2.

A beam of homogeneous radiation of energy E falls on a sheet of matter of infinitesimal thickness $dx$. Then the total energy of the deflected quanta will be denoted by SE $dx$, and the total energy of the recoil electrons by AE $dx$. This latter expression represents true absorption of γ-ray energy. The "total scattering coefficient" T, which is a measure of the rate at which energy is removed from the primary beam, is numerically equal to the sum of the "scattering coefficient" S and the "scattering absorption coefficient" A, thus

$$S + A = T. \tag{2.5}$$

The Compton formulæ are

$$S = n\sigma\,(1 + \alpha)/(1 + 2\alpha)^2\,;\ A = n\sigma\,\alpha/(1 + 2\alpha)^2\,;\ T = n\sigma/(1 + 2\alpha) \tag{2.6}$$

where $n$ is the number of electrons per cubic centimetre, and $\alpha$ has the same significance as above.

$$\sigma = \tfrac{8}{3}\pi e^4/m^2c^4 = 6\cdot 64\ .\ 10^{-25}.$$

is the classical value of the scattering coefficient.

## § 3. *The Ionisation produced in an Electroscope.*

It is now widely recognised that the ionisation produced in an electroscope by γ-rays is in general a function not only of the energy of the beam but also of the wave-length of the radiation and the material of the walls of the electroscope. The matter has recently been investigated experimentally by Chalmers.†

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* 'Roy. Soc. Proc.,' A, vol. 111, p. 405 (1926).

† 'Phil. Mag.,' vol. 6, p. 745 (1928).

In the experimental investigation of the absorption of penetrating radiation, the observed ionisation usually comprises contributions from β-particles generated in several different media. Thus, in the experiments of Millikan and Cameron there will be small contributions to the ionisation from β-particles generated in the air inside the electroscope, and in the walls of the electroscope, while the greater part of the ionisation will be due to β-particles originating in the surrounding medium. Their experiments show that the observed ionisation is not sensibly altered when the surrounding medium changes from air to water.

Hoffmann* and, more recently, Myssowsky and Tuwim† have investigated the effect of surrounding an electroscope with increasing thicknesses of lead. Comparing the absorption curve obtained in this way with curves obtained by immersing the electroscope in water, or surrounding it with ice, the latter authors find that the absorption is abnormally rapid during the first 9 cm. of lead. After 9 cm. the absorption coefficient per electron was found to be the same as that in water at an equivalent depth. The initial abnormality has been ascribed to the difference in the ratio of the absorption coefficients of primary and scattered radiations in lead and water (since the softer components of the scattered radiation will suffer photoelectric absorption in lead) leading to a change in the proportions of these radiations accompanying the transition from one medium to another. Though such a disturbance in the equilibrium between primary and degraded radiation is to be expected, a quantitative explanation of the abnormal absorption coefficients is only possible if the proportion of soft secondary radiation is much greater than the estimates reached subsequently in this paper, and based either on the Compton, Dirac, or Klein-Nishina formulæ.

It seemed worth while, therefore, to consider in some detail the extent to which the surrounding medium may influence directly the ionisation produced in an electroscope by changing the number and velocity distribution of the ionising particles. We shall see that the surrounding medium will not be without influence on the ionisation unless the rate of loss of energy of a β-particle of given velocity depends only on the number of electrons per unit volume of the medium.

Regarding the ionisation as made up of the contributions from recoil electrons emerging from the walls in all directions with a wide range of velocities, and partially "reflected" at the other walls, the problem seems so hopelessly

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[*] 'Ann. Physik,' vol. 82, p. 413 (1927).

[†] 'Z. Physik,' vol. 50, p. 273 (1928).

complicated as to be outside the scope of theoretical investigation.* Fortunately the problem may be attacked from another angle if we make the following assumption :—

That a β-particle traversing a solid medium loses the same amount of energy in travelling a distance $\Delta x$ short compared with its range, as it would do in traversing $\rho\Delta x$ of air where $\rho$ is a proportionality factor which is independent of the velocity of the particle.

Consider a small air cavity in an extended solid medium traversed by penetrating radiation in any arbitrary manner, the variations in intensity of the radiation in distances comparable with the dimensions of the cavity being negligible.

*The Ionisation due to β-Particles generated in the Walls of the Cavity.*—A priori it might be expected that the existence of the air cavity will disturb the distribution of β-particles, as regards velocity and direction, in its neighbourhood. Supposing, however, that it can be shown that this is not so, let the number of β-particles crossing any element of area $\alpha$ and lying within a cone of solid angle $\delta\omega$ of which the axis is normal to $\alpha$ and lies in the direction $(\theta, \phi)$ be

$$dN = \alpha f(\theta, \phi)\,\delta\omega. \tag{3.1}$$

Then we may calculate the contribution to the total ionisation from recoil electrons generated in the solid as follows :—

Consider on the one hand a small air cavity of any shape (A) and on the other a geometrically similar volume element of solid (B) whose linear dimensions are smaller than those of the air cavity in the ratio $\rho : 1$, where $\rho$ is the constant referred to above. Crossing any element of surface of (A) of area $\alpha$ and lying within a cone of solid angle $\delta\omega$ whose axis is in a given direction $(\theta, \phi)$ there will be a number of β-particles given by

$$dN = \alpha \cos\psi f(\theta, \phi)\,\delta\omega, \tag{3.2}$$

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* *Note added in proof*—Since this paper was communicated, a Doctorate Thesis by M. Bruzau (Paris, Nov. 1928) has come to my notice, in which the problem has been attacked in this way. After making certain simplifying assumptions the conclusion is reached that the ionisation produced by radiation of a given wave-length in a small chamber is proportional to the energy absorbed per unit volume of the material of the walls, but the proportionality factor is left undetermined. M. Bruzau has also investigated theoretically the growth of "degraded" penetrating radiation, considering only once-scattered quanta. On the basis of the Compton formulæ he finds that the apparent absorption coefficient of a parallel beam of radiation, initially homogeneous will be equal to the total scattering coefficient T of the primary radiation at great depths, but should decrease with altitude, approaching zero at the top of the atmosphere (see § 5 of this paper).

where $\psi$ is the angle between the axis of the cone and the normal to the surface at the point considered. If this group of particles travels a distance $l$ before reaching the opposite wall of the cavity, the total energy lost will be

$$dE = \alpha \cos \psi f(\theta, \phi)\, \delta\omega \,.\, l \Delta E\, F(\theta, \phi) \qquad (3.3)$$

where $\Delta E \,.\, F(\theta, \phi)$ is the energy lost per centimetre in air by particles of the particular velocity distribution appropriate to the direction $(\theta, \phi)$.

On reaching the opposite wall of the cavity, some of these particles will be "reflected" (that is, they will be scattered back into the cavity after penetrating a short distance into the solid wall) and will therefore make a further contribution to the ionisation in the cavity. This additional amount of energy, however, must not be included in $dE$, since on reaching the walls after crossing the cavity once a $\beta$-particle loses its identity. In equation (3.2), therefore, $dN$ is composed partly of $\beta$-particles which are crossing the surface for the first time, and partly of particles which have already crossed the cavity but have been so scattered by the solid as to fall within the beam considered.

In the volume element of solid (B) considering the corresponding element of surface $\alpha'$

$$dN' = \alpha' \cos \psi f(\theta, \phi)\, \delta\omega,$$

and similarly

$$dE' = \alpha' \cos \psi f(\theta, \phi)\, \delta\omega \,.\, l'\, \Delta E'\, F(\theta, \phi), \qquad (3.4)$$

where $l'$ and $\Delta E'$ have the same significance as above but with reference to solid instead of air.

Therefore since $l \Delta E = l' \Delta E'$ according to our fundamental assumption, and $\alpha = \rho^2 \alpha'$ from geometrical considerations

$$dE = \rho^2 dE'. \qquad (3.5)$$

Integrating to obtain the total energy lost by all the $\beta$-particles crossing the cavity and the volume element respectively,

$$E = \rho^2 E'. \qquad (3.6)$$

*The Ionisation due to $\beta$-Particles generated in the Air in the Cavity.*—Considering now particles generated on the one hand by the scattering of $\gamma$-rays in the air in the cavity (A) and on the other hand by $\gamma$-rays scattered in the volume element (B). Particles originating in "equivalent positions" in the gas and the solid will lose the same amount of energy in reaching the walls or escaping from the volume element. But the ratio of the volumes of (A) and (B) is $\rho^3 : 1$, so that the ratio of the number of particles generated in the two cases will be as

$$\rho^3 n_A : n_B$$

when $n_A$ and $n_B$ are the number of electrons per cubic centimetre of air and solid respectively.

Since $n_B/n_A$ is of the order of $\rho$, if the contribution to the ionisation from radiation absorbed in the air in the cavity is not more than a few per cent. of the whole, we may write for this contribution also

$$E = \rho^2 E'.$$

In the case of an electroscope of 1 or 2 litres capacity filled with air under normal pressure, the contribution to the total ionisation of β-particles generated by the scattering of penetrating radiation in the air inside the electroscope is probably less than 1 per cent. so that the criterion is satisfied. Thus, since the volumes of (A) and (B) are in the ratio $\rho^3 : 1$ we arrive at the simple relation that:—

The energy lost per unit volume by β-particles in the cavity is $1/\rho$ times the energy lost by γ-rays per unit volume of the solid.

This will be referred to as the Principle of Equivalence.

*The Influence of the Cavity on the Character of the β-Radiation.*—This simple relation has been obtained by supposing that the introduction of an air cavity into the solid has not altered the distribution, as regards velocity and direction, of the β-particles crossing the boundary surface of the cavity. We proceed to examine this assumption.

The β-particles crossing any element of area of the cavity surface inwards fall into two groups:—

(*a*) Those β-particles generated in the vicinity of the area and crossing the surface for the first time.

(*b*) Those particles which, coming from the rest of the cavity surface, have crossed the cavity and been scattered in such a manner as to pass through the area considered.

Obviously, before the introduction of the cavity (*i.e.*, in a uniform mass of solid) a group of particles identical with (*a*) will cross the same area. Instead of (*b*) there will be another group of particles (*c*) generated in the vicinity of the area. We have to consider the equivalence of (*b*) and (*c*). Since the velocity and angular distribution of the "reflected" particles is determined uniquely by that of the particles travelling outwards across the cavity wall, it is sufficient to show that this latter distribution is unaltered by the introduction of the cavity. The equivalence may be established by the method of induction.

Suppose that the distribution of the particles travelling outwards over the whole cavity wall except a certain elementary area $\delta\alpha$ is undisturbed, then we may find the distribution of particles crossing this area outwards as follows.

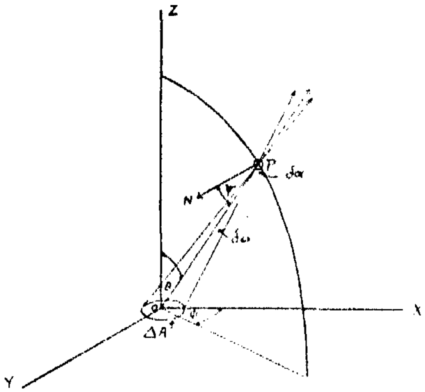

FIG. 3.

Those particles crossing the area of cavity surface $\Delta A$ in the XY plane have the normal distribution, so that the number of particles lying within a cone of solid angle $\delta\Omega$ whose axis is in the direction $(\theta, \phi)$ is given by

$$dN = \Delta A \cos\theta f(\theta, \phi)\, \delta\Omega. \qquad (3.7)$$

Let $\delta\Omega$, $\theta$, $\phi$ be so chosen that this cone cuts the surface of the cavity again in the element of area $\delta\alpha$ at P, this being the element of area under consideration. The normal PN to $\delta\alpha$ makes an angle $\psi$ with PO. Then if $PO = r$

$$\delta\Omega = \delta\alpha \cos\psi / r^2,$$

therefore

$$dN = \delta\alpha \cos\psi f(\theta, \phi)\, \Delta A \cos\theta / r^2 = \delta\alpha \cos\psi f(\theta, \phi)\, \delta\omega, \qquad (3.8)$$

where $\delta\omega$ is the solid angle of the cone having its vertex at P and which intersects the cavity wall in $\Delta A$. If we neglect the scattering of the $\beta$-particles by the air in the cavity, all particles lying originally within this cone will cross the area $\delta\alpha$.

But the expression

$$\delta\alpha \cos\psi f(\theta, \phi)\, \delta\omega$$

is equal to the number of particles which would cross $\delta\alpha$ outwards in the direction $(\theta, \phi)$ and lying within $\delta\omega$ if it were situated in a continuous medium. Since $\Delta A$ was any portion of the cavity surface, this statement is true for all the $\beta$-particles crossing the area $\delta\alpha$ outward and hence also it is true generally that the distribution as regards velocity and direction of the particles crossing the boundary of the cavity is not disturbed by the replacement of the solid inside the boundary by air. The scattering of $\beta$-particles in crossing the cavity has been neglected, a procedure which is obviously justifiable if the dimensions of the cavity be sufficiently small, but not necessarily so in the case of an electroscope of linear dimensions of the order of 10 cm. Experimenting with a small ionisation chamber of graphite of 1 or 2 c.c. capacity, I have found that the ionisation due to radium (B + C) $\gamma$-rays varies linearly with the pressure between 2 and 76 cm. of mercury. Since the scattering varies with the pressure, it is evident that though the angular distribution of the $\beta$-particles may be altered the resultant influence on the ionisation is negligible for such a chamber. Millikan* observed that the relation between pressure and ionisation in his electroscopes was roughly linear between 1 and 8 atmospheres, but has published no details as to the extent of the variation. He observed previously† that results obtained with two electroscopes of 2 litres and 3 litres capacity respectively differed by amounts varying between 1 per cent. and 5 per cent. in different localities. These electroscopes were made of steel, the thickness of the walls being 2 mm. and 3 mm. respectively. Now the order of magnitude of the range of the recoil electrons produced by penetrating radiation is 15 gm. per square centimetre, *i.e.*, 2 cm. of steel or 100 metres of air, so that the majority of the particles will have originated outside the electroscope, and the difference in wall thickness can hardly have influenced the ionisation to a greater extent than a few per cent.

*Application of the Principle of Equivalence to the Case of an Electroscope.*—It is evident that the ionisation produced in an electroscope will vary with the nature of the surrounding medium, being in fact a function of $\rho n/n_A$, where $\rho$ as usual is the ratio of the rate of loss of energy with distance of $\beta$-particles traversing the medium and traversing air, and $n$ and $n_A$ are the number of electrons per cubic centimetre in the two media. In the limiting case of the ionisation produced in air, other media being far removed, the principle of equivalence leads to the value for the number of ions produced per cubic centimetre per second :—

$$N = E\,A/W, \qquad (3.9)$$

where E is the flux of energy in the form of penetrating radiation, A is the scattering absorption coefficient of the radiation (equation (2.5) and W the mean energy required to produce a pair of ions.

The foregoing discussion leads us to expect that the ionisation in a thin walled electroscope (up to 1 gm. per square centimetre) will not differ markedly from this value as long as the electroscope is situated in air. The presence of other media, and particularly a lead shield surrounding the electroscope, probably influences the magnitude of the ionisation very considerably.

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* Millikan and Cameron, 'Phys. Rev.,' vol. 31, p. 921 (1928).

† Millikan and Cameron, 'Phys. Rev.,' vol. 31, p. 163 (1928).

### § 4. *The Ionisation produced by Degraded Radiation.*

Whenever a primary quantum of energy E is scattered there is produced a recoil electron, the energy of which is transformed into "primary" ionisation and a quantum of "degraded" $\gamma$-ray energy, the whole of which is ultimately transformed into degraded ionisation. On the average the primary energy E gives rise to energy of recoil electrons of amount AE, and degraded radiation of amount SE. Thus corresponding to the complete absorption of a homogeneous beam of radiation, we have

$$\frac{I_P}{I_D} = \frac{\text{Total Primary Ionisation}}{\text{Total Degraded Ionisation}} = \frac{A}{S}, \tag{4.1}$$

where A and S are the coefficients defined above (§ 2). According to the Compton formulæ, for the wave-lengths under consideration $A = S$, while the new Klein-Nishina formula leads to $A \triangleq 4S$. It is evident therefore that these formulæ will lead to very different results for the relative magnitude of primary and degraded ionisation at any point, and that the latter may be of considerable importance. In order to ascertain how the existence of the degraded ionisation will influence the apparent absorption coefficient of the beam, it is necessary to proceed with a more detailed calculation. It is evident that the degraded radiation will build up from the primary in a manner analogous to the growth of a short-lived radioactive substance from a decaying parent body. After equilibrium has been reached the total ionisation $J = I_P + I_D$ will fall off in a manner identical with the absorption of the primary radiation alone. Whether or not experimental absorption curves may be used as the basis of calculation of wave-lengths will therefore depend upon how quickly equilibrium is reached between degraded and primary ionisation.

### § 5. *The Characteristics of Degraded Radiation.*

If the suffixes 0 and 1 refer to primary and once scattered quanta respectively, then considering average values

$$\lambda_1 = \lambda_0 T_0/S_0, \tag{5.1}$$

since $S_0$ is proportional to the energy and $T_0$ to the number of scattered quanta.

The mean direction of emission is given by (2.4)

$$1 - \cos\theta = \frac{mc}{h}(\lambda_1 - \lambda_0) = \frac{mc}{h}\lambda_0\left(\frac{T_0}{S_0} - 1\right). \tag{5.2}$$

Assuming, as a typical case $\lambda_0 = 0{\cdot}00048$ Å.U., we find, using the Compton formulæ (2.6) :—

| | | |
|---|---|---|
| $\lambda_1 = 0{\cdot}00096$ | $\theta_1 = 11^\circ$ | $\cos\theta_1 = 0{\cdot}98$ |
| $\lambda_2 = 0{\cdot}00188$ | $\theta_2 = 16^\circ$ | $\cos\theta_2 = 0{\cdot}96$ |
| $\lambda_3 = 0{\cdot}00351$ | $\theta_3 = 21^\circ$ | $\cos\theta_3 = 0{\cdot}93$ |
| $\lambda_4 = 0{\cdot}00657$ | $\theta_4 = 29^\circ$ | $\cos\theta_4 = 0{\cdot}87$ |
| $\lambda_5 = 0{\cdot}01177$ | $\theta_5 = 38^\circ$ | $\cos\theta_5 = 0{\cdot}79$ |

We observe that at each scattering process the wave-length is approximately doubled. In the calculations which follow it is assumed that the scattered quanta travel straight forward ($\theta = 0$), thus involving an error of the order of $(1 - \cos\theta)$.

It is convenient to adopt the "equivalent metre of water" as the unit of distance, this being the thickness of the medium under consideration which contains the same number of electrons per square centimetre as 1 metre of water. Distances are measured downwards from the top of the atmosphere.

*The Primary Ionisation.*—Consider first the primary ionisation due to homogeneous isotropic penetrating radiation of density $N_0 h\nu_0$ at the top of the earth's atmosphere. At a depth $x$ the energy arriving within the solid angle $\sin\theta\, d\phi\, d\theta$ is

$$dE = N_0 h\nu_0 \sin\theta\, d\phi\, d\theta\, e^{-T_0 x \sec\theta}.$$

By (3.9) the corresponding ionisation is

$$dI = A_0 \,.\, N_0 h\nu_0 \sin\theta\, d\phi\, d\theta\, e^{-T_0 x \sec\theta},$$

where $I = NW$ is referred to for brevity as the ionisation.

Hence integrating with respect to $\phi$ and $\theta$ the total primary ionisation at a depth $x$ is

$$I_0 = N_0 h\nu_0 A_0 \int_0^{2\pi}\int_0^{\frac{1}{2}\pi} \sin\theta\, e^{-T_0 x \sec\theta}\, d\phi\, d\theta$$

$$= 2\pi N_0 h\nu_0 A_0 \int_0^{\frac{1}{2}\pi} \sin\theta\, e^{-T_0 x \sec\theta}\, d\theta.$$

Substituting $2\pi N_0 h\nu_0 = K$ and $\sec\theta = Z$ we have

$$I_0 = A_0 K \int_1^\infty \frac{e^{-T_0 x Z}}{Z^2}\, dZ = A_0 K\, [e^{-T_0 x} + T_0 x\, Ei\,(-T_0 x)],$$

where

$$Ei\,(-T_0 x) = \int_\infty^{T_0 x} \frac{e^{-u}}{u}\, du$$

is the value of the "exponential-integral" between the limits $\infty$ and $T_0x$ and has been evaluated by Glaisher.*

Denoting $[e^{-T_0x} + T_0x\,Ei(-T_0x)]$ by $F(T_0x)$ we have

$$I_0 = A_0KF(T_0x). \tag{5.3}$$

*The Degraded Ionisation.*—Consider now the ionisation due to once scattered radiation at any point P at a depth $x$ equivalent metres below the top of the atmosphere. Taking P as the origin of polar co-ordinates, the amount of energy lying within the solid angle $\sin\theta\, d\phi\, d\theta$ which is scattered in the volume element $r^2 \sin\theta\, d\phi\, d\theta\, dr$ is

$$N_0h\nu_0 \sin\theta\, d\phi\, d\theta\, dr\, e^{-T_0(R-r)}\, S_0,$$

where $R = x \sec\theta$.

Since this scattered energy is assumed to travel in the direction of the primary radiation, the energy reaching P in the direction considered is

$$dE = \int_0^R S_0 . N_0h\nu_0 \sin\theta\, d\phi\, d\theta\, e^{-[T_0(R-r)+T_1r]}\, dr$$

$$= \frac{S_0N_0h\nu_0}{T_1-T_0} \sin\theta\, [e^{-T_0R} - e^{-T_1R}]\, d\phi\, d\theta. \tag{5.4}$$

Multiplying by $A_1$ and integrating with respect to $\phi$ and $\theta$ we find

$$I_1 = \frac{2\pi N_0h\nu_0S_0A_1}{T_1-T_0}[F(T_0x) - F(T_1x)] = K\frac{S_0A_1}{T_1-T_0}[F(T_0x) - F(T_1x)], \tag{5.5}$$

whence

$$\frac{I_1}{I_0} = \frac{S_0}{T_1-T_0}\frac{A_1}{A_0}\left[1 - \frac{F(T_1x)}{F(T_0x)}\right].$$

Proceeding in a similar way to obtain the ionisation due to twice scattered radiation, we have—

The amount of once scattered radiation which suffers a second scattering process in the volume element $r^2 \sin\theta\, d\phi\, d\theta\, dr$ so as to reach P is (*cf.* equation 5.4)

$$\frac{N_0h\nu_0S_0}{T_1-T_0} \sin\theta\, [e^{-T_0r} - e^{-T_1r}]\, d\phi\, d\theta\, S_1\, dr.$$

Therefore the ionisation at P due to this radiation is

$$I_2 = \int_0^{2\pi}\int_0^{\frac{1}{2}\pi}\int_0^R A_2 e^{-T_2(R-r)} \frac{N_0h\nu_0S_0}{T_1-T_0} \sin\theta\, [e^{-T_0r} - e^{-T_1r}]\, S_1\, d\phi\, d\theta\, dr,$$

or

$$I_2 = 2\pi N_0h\nu_0 \frac{S_0S_1A_2}{T_1-T_0}\left[\frac{F(T_0x)}{T_2-T_0} - \frac{F(T_1x)}{T_2-T_1} + \frac{(T_1-T_0)\,F(T_2x)}{(T_2-T_0)(T_2-T_1)}\right] \tag{5.6}$$

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* 'Phil. Trans.,' vol. 160, p. 367 (1870).

so that

$$\frac{I_2}{I_0} = \frac{S_0}{T_1 - T_0} \cdot \frac{S_1}{T_2 - T_0} \cdot \frac{A_2}{A_0}\left[1 - \frac{T_2 - T_0}{T_2 - T_1}\frac{F(T_1x)}{F(T_0x)} + \frac{T_1 - T_0}{T_2 - T_1}\frac{F(T_2x)}{F(T_0x)}\right].$$

When $x$ is very large the expression inside the brackets approaches unity, so that we can write down at once the ratio

$$\frac{I_n}{I_0} = \frac{S_0}{T_1 - T_0} \cdot \frac{S_1}{T_2 - T_0} \cdot \frac{S_2}{T_3 - T_0} \cdots \frac{S_{n-1}}{T_n - T_0} \cdot \frac{A_n}{A_0}. \tag{5.7}$$

The total ionisation $J = I_0 + I_1 + \ldots I_n$ is an expression of the form

$$J = P_0F(T_0x) + P_1F(T_1x) + P_2F(T_2x) + \ldots .$$

Differentiating with respect to $x$, it may be shown that the apparent absorption coefficient is given by

$$\mu = -\frac{1}{J}\frac{dJ}{dx} = \frac{1}{x}\left[\frac{P_0e^{-T_0x} + P_1e^{-T_1x} + \ldots}{J} - 1\right]. \tag{5.8}$$

## § 6. *The Curves.*

Following the method outlined in the preceding paragraph depth-ionisation curves have been computed on the basis of the Compton formulæ for primary radiation of wave-length corresponding to a total scattering coefficient $T_0$ of 0·22 metre$^{-1}$ for water, which is the order of magnitude of the experimentally observed absorption coefficient of the softer components of penetrating radiation.

*The Curves based on the Compton Formulæ.*—Fig. 4 shows the growth of degraded ionisation. The ionisation produced by radiation of successive stages of degradation is expressed as a fraction of the primary ionisation at the same point. On the extreme right of the figure (depth $= \infty$) the equilibrium values of the ionisation are shown, and it is evident that the degraded ionisation will have reached 85 per cent. of its equilibrium value in the first 7 "equivalent metres" of atmosphere, that is, at an altitude of about 3000 metres, since the depth of sea level is 10·4 equivalent metres under normal barometric pressure.

In fig. 6, the curve marked "degraded" refers to the sum of the ionisations produced by all the degraded radiations. As was pointed out in § 4 (equation 4.1) the area under the curve marked "primary" should be to the area under that marked "degraded" in the ratio of the coefficients A and S of the primary radiation. The curves shown satisfy this numerical check.

The absorption of the primary radiation is not exponential because we are not dealing with a parallel beam but with radiation which is initially isotropic.

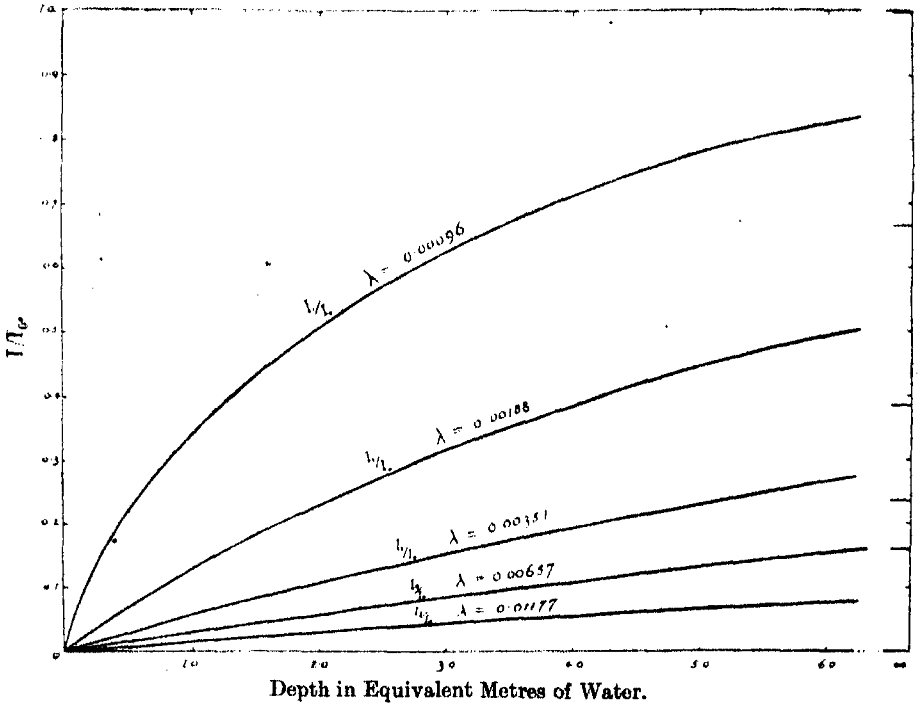

FIG. 4.—Depth-Ionisation Curves. $T_0 = 0 \cdot 22$ metre$^{-1}$. $\lambda_0 = 0 \cdot 00048$ Å.U.

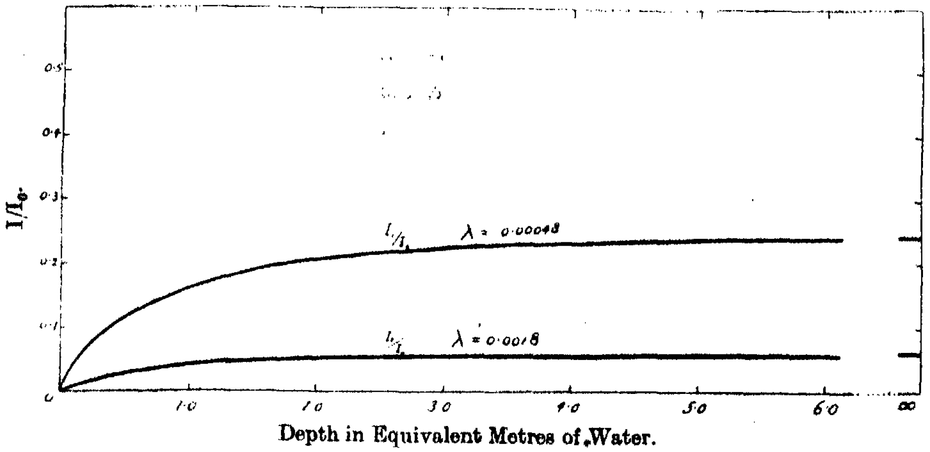

FIG. 5.—Depth-Ionisation Curves. Klein-Nishina Formulæ. $T_0 = 0 \cdot 22$ metre$^{-1}$. $\lambda_0 = 0 \cdot 000094$ Å.U.

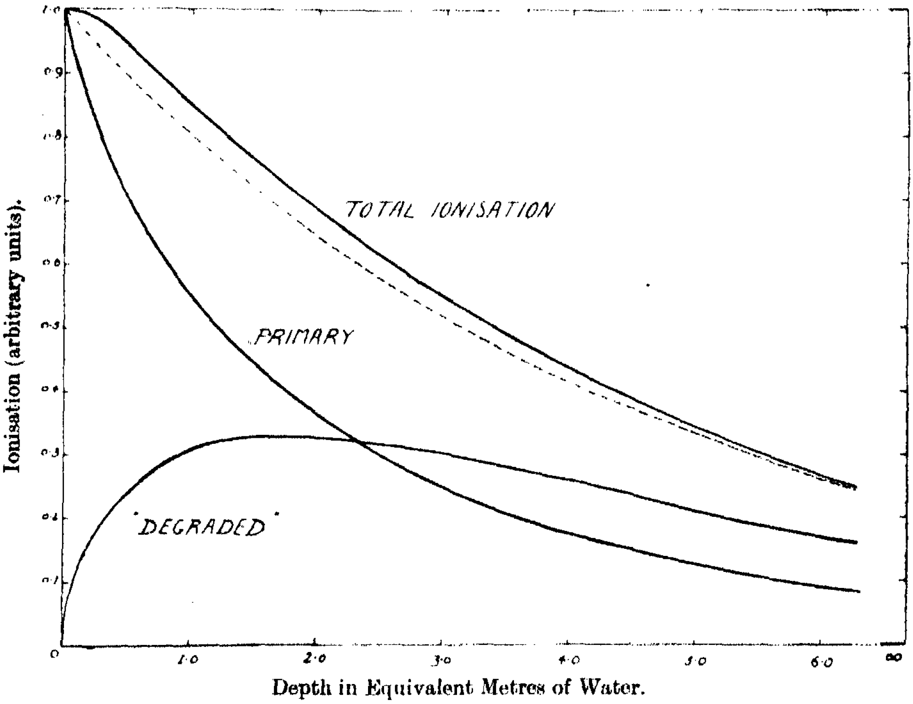

FIG. 6.—Depth-Ionisation Curves. $T_0 = 0{\cdot}22$ metre$^{-1}$. $\lambda_0 = 0{\cdot}00048$ Å.U.

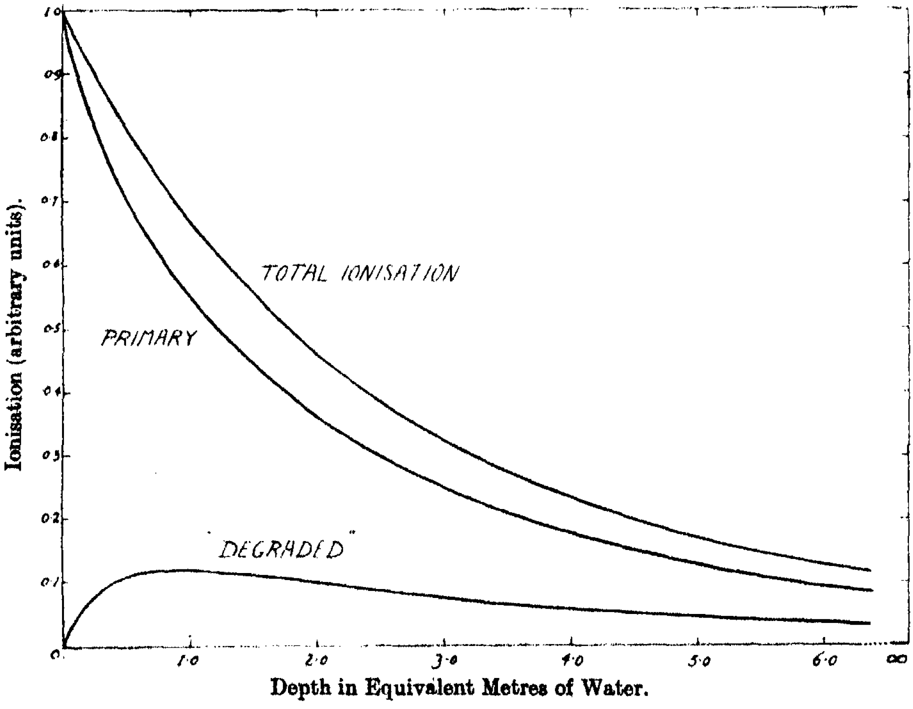

**FIG. 7.—Depth-Ionisation Curves. Klein-Nishina Formulæ. $T_0 = 0{\cdot}22$ metre$^{-1}$. $\lambda_0 = 0{\cdot}000094$ Å.U.**

It appears, however, that the total ionisation J falls off with depth in a manner which is approximately exponential, the exponent being T, the total scattering coefficient of the primary radiation. This is seen in the figure by the close proximity of the total ionisation curve, and the broken line which is the curve $J = J_0 e^{-0.22x}$. Since an approximate depth-ionisation curve for any other wave-length may be obtained from fig. 6 simply by an expansion or contraction of the abscissæ, this relation holds for all wave-lengths. It is, however, specific to the Compton scattering formulæ. Thus it is not shown in fig. 7 where the curves are computed on the basis of the Klein-Nishina formulæ.

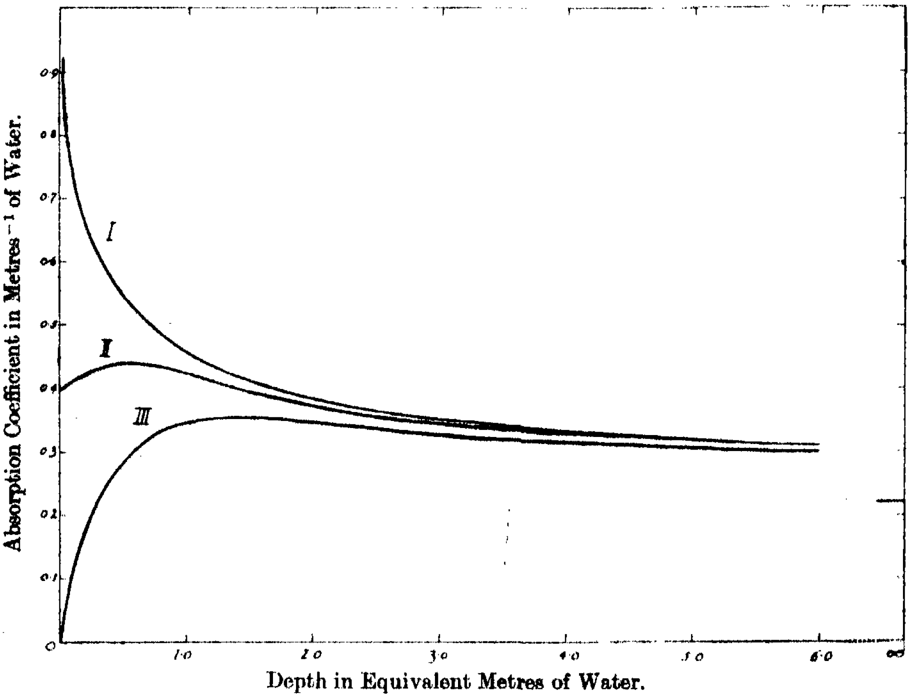

FIG. 8.—Apparent Absorption Coefficients. $T_0 = 0 \cdot 22$ metre$^{-1}$.

Curve I, fig. 8, shows the variation with depth of the apparent absorption coefficient $\mu_0 = -\frac{1}{I_0}\frac{dI_0}{dx}$ of the primary radiation alone and may be calculated accurately from (5.8) by considering only the terms in $T_0x$. This equation, however, is not suitable for computing the experimental absorption coefficient $\bar{\mu} = -\frac{1}{J}\frac{dJ}{dx}$ which therefore has been obtained by graphical methods. This quantity is plotted in Curve III which, though not accurate, is reliable in the interesting features which it reveals. Thus we are led to expect that if the penetrating radiation were initially homogeneous, the observed absorption coefficient would at first increase with altitude (due to the isotropic nature of the incident radiation) and then fall steeply to zero. Unfortunately the altitude at which the absorption coefficient would be expected to begin to decrease is so great as to be beyond the reach of mountain experiments, but the maximum might be revealed by balloon observations.

*The Curves based on the Klein-Nishina Formulæ.*—So far attention has been confined to curves based on the Compton formulæ. In figs. 5 and 7 are represented a similar set[*] of curves computed on the basis of the Klein-Nishina formulæ. The corresponding absorption coefficient $\mu = -\frac{1}{J}\frac{dJ}{dx}$ is shown in Curve II, fig. 8. Qualitatively the two sets of curves are similar, but the numerical differences between them are very great. Thus, while both sets of curves refer to primary radiation for which the total scattering coefficient T is 0·22 metre$^{-1}$, the wave-length of the primary radiation according to the Klein-Nishina formulæ is only about one-fifth of that given by the Compton formulæ. However, the mean change in wave-length at each scattering process is greater, so that after two scattering processes the wave-length is the same as that of the twice scattered radiation calculated according to the Compton formulæ. Corresponding to the more rapid degradation there is an increase in the rate at which equilibrium is reached. Thus it is seen from fig. 5 that the degraded ionisation has reached 85 per cent. of its equilibrium value after 2 metres whereas this is only attained after 7 metres according to the older theory. Whereas on the Compton formulæ the ionisation produced by degraded radiation is approximately equal to that produced by the primary radiation, according to the new formulæ it is only 20 per cent. of the primary ionisation and for the wave-length considered only the once and twice scattered radiations are of importance. This follows at once from the fact that the new formulæ yield values of A/S which are of the order of four, as compared with unity on the older formulæ (*cf.* § 4).

The following table, containing data computed on the basis of the Klein-Nishina formulæ, may be compared with that given on p. 657 :—

| | $T_0 = 0{\cdot}22$ metre$^{-1}$. | $\lambda_0 = 0{\cdot}000094$ Å.U. |
|---|---|---|
| $\lambda_1 = 0{\cdot}00048$ Å.U. | $\theta_1 = 10°$ | $\cos\theta_1 = 0{\cdot}98$ |
| $\lambda_2 = 0{\cdot}0018$ Å.U. | $\theta_2 = 20°$ | $\cos\theta_2 = 0{\cdot}94$ |

*Calculations based on the Dirac Formulæ.*—Although for a given value of the total scattering coefficient T, the Dirac formulæ lead to wave-length estimates some 30 per cent. smaller than those given by the Compton formulæ, the relative magnitudes of primary and degraded ionisation are almost identical in the two cases so that it was considered unnecessary to construct a special set of curves corresponding to the Dirac formulæ.

*Experimental Absorption Coefficients.*—Referring to fig. 8, Curve I represents the variation with depth of the quantity $\mu_0 = -\frac{1}{I_0}\frac{dI_0}{dx}$, where $I_0$ is the primary ionisation due to radiation which is initially homogeneous and isotropic at the top of the atmosphere. Curves II and III show the variation with depth, computed on the basis of the Klein-Nishina and Compton formulæ respectively, of the quantity $\bar{\mu} = -\frac{1}{J}\frac{dJ}{dx}$ where J is the total ionisation at any point produced by the same incident radiation in a thin walled electroscope surrounded by air. For the particular case $T_0 = 0{\cdot}22$ metre$^{-1}$, therefore, the difference in the ordinates of the Curves I and II, or I and III, at any given depth, is a measure of the error introduced into wave-length estimates through ignoring the ionisation produced by degraded radiation.

Since, according to the Compton formulæ (2.6), approximately

$$T_0 = \tfrac{1}{2}T_1 = \tfrac{1}{4}T_2 \ldots,$$

equation (5.8) reduces to

$$\bar{\mu} = \frac{1}{x}\left[\frac{\kappa_0 e^{-T_0x} + \kappa_1 e^{-2T_0x} + \kappa_2 e^{-4T_0x} + \ldots}{\kappa_0 F(T_0x) + \kappa_1 F(2T_0x) + \ldots} - 1\right],$$

or

$$\frac{\bar{\mu}}{T_0} = f(T_0x), \tag{6.1}$$

so that from Curve III, $\bar{\mu}$ may readily be ascertained for any wave-length by expanding the abscissæ in the ratio of the coefficients $T_0$ for the two primary radiations in question. The divergence between $\bar{\mu}$ and $\mu_0$ is obviously greatest for hard radiations and high altitudes. By an appropriate contraction of the abscissæ we find from Curve III that for $T_0 = 0{\cdot}04$ metre$^{-1}$ (the hardest radiation observed by Millikan), $\bar{\mu}$ differs from $\mu_0$ by 20 per cent. at a depth of 7 metres, *i.e.*, at an altitude of 3000 metres.

Owing to the more complicated form of the Klein-Nishina formulæ it is not possible to find the variation of $\bar{\mu}$ with depth from Curve II, fig. 8, merely by an expansion or contraction of the abscissæ. Since, however, Curve II always lies between Curves I and III the estimated difference between $\bar{\mu}$ and $\mu_0$ will always be less according to the Klein-Nishina than according to the Compton formulæ.

### § 7. *The Validity of the Klein-Nishina Formulæ.*

For the total scattering coefficient T defined in (2.5), Klein and Nishina arrive at the formulæ

$$\mathrm{T} = n\frac{\pi e^4}{m^2c^4}\,2\left\{\frac{1+\alpha}{\alpha^2}\left[\frac{2(1+\alpha)}{1+2\alpha} - \frac{1}{\alpha}\log_e(1+2\alpha)\right] + \frac{1}{2\alpha}\log_e(1+2\alpha) - \frac{1+3\alpha}{(1+2\alpha)^2}\right\}, \qquad (6.1)$$

and from the expression

$$\mathrm{J} = \mathrm{I}_0\frac{e^4}{2m^2c^4}\,\frac{1+\cos^2\theta}{\{1+\alpha(1-\cos\theta)\}^3}\left(1 + \frac{\alpha^2(1-\cos\theta)}{(1+\cos^2\theta)\{1+\alpha(1-\cos\theta)\}}\right)$$

which they find for the amount of energy I scattered per electron per unit solid angle in a direction $(\theta, \phi)$ in terms of $\mathrm{I}_0$ the incident energy per square centimetre one may obtain by integration.

$$\mathrm{S} = n\frac{\pi e^4}{m^2c^4}\left[\frac{1}{\alpha^3}\log_e(1+2\alpha) + \frac{2(1+\alpha)(2\alpha^2-2\alpha-1)}{\alpha^2(1+2\alpha)^2} + \frac{8\alpha^2}{3(1+2\alpha)^3}\right], \qquad (6.2)$$

where as usual $\alpha = h\nu/mc^2$, and $n$ is the number of electrons per cubic centimetre. For radiation having an absorption coefficient $\mathrm{T} = 0{\cdot}35$ metre$^{-1}$ in water, $\alpha$ is of the order 200, so that these two equations may, with sufficient accuracy, be written

$$\mathrm{T} = n\frac{\pi e^4}{m^2c^4}\cdot\tfrac{8}{3}\cdot\frac{1}{2\alpha}\{\tfrac{3}{8} + \tfrac{3}{4}\log_e 2\alpha\}, \quad \mathrm{S} = n\frac{\pi e^4}{m^2c^4}\cdot\tfrac{8}{3}\cdot\frac{1}{4\alpha}\cdot 2. \qquad (6.3)$$

These may be compared with the Compton formulæ (for large values of $\alpha$)

$$\mathrm{T} = n\frac{\pi e^4}{m^2c^4}\cdot\tfrac{8}{3}\cdot\frac{1}{2\alpha}, \quad \mathrm{S} = n\frac{\pi e^4}{m^2c^4}\cdot\tfrac{8}{3}\cdot\frac{1}{4\alpha}.$$

The nearest approach to a simple and direct comparison between theory and experiment would be obtained by a study of the absorption and scattering of thorium C″ γ-rays since it is estimated that about 80 per cent. of the energy of this radiation is contained in the line $\lambda = 0{\cdot}0047$ Å.U. Unfortunately, the experimental data concerning these rays are very meagre. The most recent determination of the total scattering coefficient in aluminium appears to be that made by Rutherford and Richardson* in 1913 who obtained $\mathrm{T}_{\mathrm{Al}} = 0{\cdot}096$ cm.$^{-1}$. Assuming that all the energy resided in the one line, the theoretical formulæ give $\mathrm{T} = 0{\cdot}047$ (Compton), $\mathrm{T} = 0{\cdot}056$ (Dirac), $\mathrm{T} = 0{\cdot}097$ cm.$^{-1}$

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* 'Phil. Mag.,' vol. 26, p. 917 (1913).

(Klein-Nishina). The exact agreement between experiment and the Klein-Nishina formula must be fortuitous. Nevertheless when experimental data referring to radium (B + C) $\gamma$-rays are made the basis of other comparisons the new formulæ are in general in close agreement with experiment, whereas the formulæ of Compton and Dirac may be more than 30 per cent. in error. Skobelzyn* has observed the velocity and direction of emission of recoil electrons produced by radium (B + C) $\gamma$-rays (filtered through 3-mm. lead) in a Wilson Cloud chamber. Using the new scattering formulæ one may deduce from these observations the spectral distribution of the $\gamma$-ray energy, and hence compute the theoretical absorption coefficient of the $\gamma$-rays in aluminium. One finds $T_{Al} = 0\cdot155$ cm.$^{-1}$ if one makes an approximate correction for the lack of proportionality between the ionisation produced in an aluminium electroscope and the energy of the radiation, by weighing each wave-length by the corresponding value of A, the scattering absorption coefficient (*cf.* § 3). Probably the best experimental value is $T = 0\cdot162$ cm.$^{-1}$. The values of $T_{Al}$ estimated by the Compton and Dirac formulæ (using these formulæ to derive the spectral distribution as well as to estimate the absorption coefficients) are respectively 25 per cent. and 20 per cent. too low. When radium C $\gamma$-rays are filtered through 4 cm. of lead a considerable proportion of the energy of the filtered rays is found in the line $\lambda = 0\cdot00695$ Å.U. and the remaining energy, according to rough estimates, is more or less equally distributed about this line. The three theoretical coefficients are $T_{Al} = 0\cdot066$ (Compton), $T_{Al} = 0\cdot077$ (Dirac), and $T = 0\cdot123$ cm.$^{-1}$ (Klein-Nishina), while the experimental value is $0\cdot125$ cm.$^{-1}$

The experimental data concerning the angular distribution of scattered $\gamma$-radiation are hardly sufficiently precise to warrant comparison with theory.

The angular distribution in the direction of emission of recoil electrons, however, was studied by Skobelzyn using the same $\gamma$-ray beam as that from which the spectral distribution has been deduced. In order to make a valid comparison with theory, the relative number of tracks contributed by each line in the three angular ranges 0°–30°, 30°–60°, 60°–90°, has been calculated using the Klein-Nishina formulæ, and summed to obtain the theoretical distribution :—

| | 0°–30°. | 30°–60°. | 60°–90°. |
|---|---|---|---|
| **Observed (Skobelzyn)** ........................ | **176** | **144** | **88** |
| **Calculated (Klein-Nishina)** .................. | **174** | **159** | **75** |

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* 'Z. Physik.,' vol. 43, p. 354 (1927).

Since the experimental figures refer to the actual number of tracks observed, the discrepancy between theory and experiment is just outside the "probable error," but is hardly sufficient to constitute a serious challenge to the validity of the new formulæ.

The alteration in wave-length estimates introduced by interpreting absorption coefficients in terms of the new formulæ is seen from the following table :—

| Total scattering coefficient T in metres$^{-1}$ of water. | | 0·35. | 0·08. | 0·04. |
|---|---|---|---|---|
| Energy of quantum in electron-volts | Compton | 16·3 . $10^6$ | 71·4 . $10^6$ | 143 . $10^6$ |
| | Dirac | 24·5 . $10^6$ | 107 . $10^6$ | 214 . $10^6$ |
| | Klein-Nishina | 90 . $10^6$ | 360 . $10^6$ | 920 . $10^6$ |

It seems likely on theoretical grounds that whenever a system emits an amount of energy E, its mass is diminished by $E/c^2$ where $c$ is the velocity of light. From the table we see that if the smallest absorption coefficient observed with certainty is interpreted in terms of the Klein-Nishina formulæ it corresponds to a quantum of energy 9·2 . $10^8$ε-volts. The production of such a quantum would involve the annihilation of mass almost exactly equal to the mass of a proton. Conversely, if such a quantum is scattered through 180° by an electron, all but a negligible fraction of its energy is transferred to the electron which thereby acquires a mass of the same order as that of the proton.

### *Summary.*

Adopting the hypothesis that penetrating radiation is a type of γ-radiation, its absorption in the atmosphere is investigated from the theoretical standpoint.

1. An attempt is made to establish a quantitative correlation between the ionisation produced in an electroscope by penetrating radiation and the scattering absorption coefficient of the radiation.

2. The relative magnitudes of the ionisation produced by primary and scattered radiations at any point are computed by approximate methods. The calculations are made on the basis of the Compton scattering formulæ, and also on the basis of the new scattering formulæ proposed by Klein and Nishina.

3. On the basis of these results the relation between the apparent absorption coefficient of a homogeneous isotropic radiation and the true scattering coefficient of the primary radiation is discussed.

4. The adequacy of the Klein-Nishina formulæ to account for the observed absorption and scattering of γ-rays is briefly considered.

I wish to express my thanks to Sir Ernest Rutherford and Mr. R. H. Fowler for the interest they have taken in this work, and to Mr. H. J. J. Braddick for many helpful suggestions as to the mode of presentation. I am also indebted to the Department of Scientific and Industrial Research for a maintenance grant.

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# *An Investigation of the Ranges of the Long Range α-Particles from Thorium C and Radium C, using an Expansion Chamber.*

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[PLATES 11, 12.]

## *Introduction.*

The existence of the so-called long range α-particles was first pointed out by Rutherford and Wood,* who found, when observing scintillations caused by α-particles from thorium active deposit, that particles were present of ranges estimated as 10·2 and 11·3 cm. in air† at 760 mm. and 15° C. Later work, both by Rutherford‡ and by Wood§ in 1921, showed that these long range particles were α-particles coming from the source, and in view of the possible theoretical importance of these results, Bates and Rogers|| in 1923–24 made an intensive search for long range particles of all ranges. From thorium C they found in all three groups, one at 11·5 cm. and two of greater range at 15·0 and 18·4 cm. respectively, but their methods were open to serious objection, and later experiments by Yamada¶ yielded certain evidence of one group only, that at 11·5 cm. Up to this point only scintillation methods had been employed, but in 1926 Meitner and Freitag** published an account of some

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* 'Phil. Mag.,' vol. 31, p. 379 (1916).

† Air under these conditions is referred to throughout this paper as standard air.

‡ 'Phil. Mag.,' vol. 41, p. 570 (1921).

§ 'Phil. Mag.,' vol. 41, p. 575 (1921).

|| 'Roy. Soc. Proc.,' A, vol. 105, p. 97 (1924).

¶ 'J. Physique,' vol. 6, p. 380 (1925).

** 'Z. Physik,' vol. 37, p. 481 (1926).

experiments on these long range particles in which an expansion chamber was used. They detected a group of particles at 11·5 cm. in standard air and also another group at 9·5 cm. Philipp,* using the scintillation method, was also able to detect the 9·5 cm. particles and obtained results agreeing closely in all respects with those of Meitner and Freitag.

The long range particles from radium active deposit were first observed by Rutherford† in 1919 and were subsequently studied by Bates and Rogers (*loc. cit.*), who in this case also found three groups of long range particles, with ranges 9·3, 11·2 and 13·3 cm. in air. In 1924, also, Rutherford and Chadwick‡ gave an account of a very thorough investigation of the long range particles from radium active deposit. They showed that the particles arose from radium C or its products and that those of range 9·3 cm. were certainly α-particles. They also found a group of range 11·2 cm. containing approximately one-sixth as many particles as were contained in the 9·3 cm. group.

A little later Yamada (*loc. cit.*) reported the results of his experiments on the long range α-particles from radium C but in this case he detected only particles of 9·3 cm. range.

More recently Philipp§ investigated these particles using an expansion chamber but only twenty-six long range tracks were photographed. Of these four had ranges between 9·5 and 12 cm.

## *Survey of Methods of Range Measurement as Applied to Long Range Particles.*

Though there are some obvious objections to the use of the scintillation method for the above purpose, it is the method which has been most frequently employed in determining the ranges of the long range particles. The method theoretically yields a curve giving number of α-particles with range greater than R against R, but actually before such a curve can be drawn a smoothing process is necessary in order to eliminate irregularities due to probability fluctuations in the emission of the particles; and even after this has been done the curve obtained does not give ranges as accurately as its derivative curve (number of particles with ranges between R and $R + \Delta R$ against R). In addition, counting becomes very difficult when observing the low velocity particles at the end of the range, and so this number distance curve must be considerably distorted just where it is required to be most accurate. The custom has been to obtain from such a scintillation curve an extrapolated range, but, on examining the justification for this procedure, it is seen that even if the scintillation measurements were reliable, the range obtained would depend upon the straggling coefficient of the medium through which the particles had passed as well as upon the actual mean range of the particles.

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* 'Z. Physik,' vol. 37, p. 518 (1926).

† 'Phil. Mag.,' vol. 37, p. 571 (1919).

‡ 'Phil. Mag.,' vol. 48, p. 509 (1924).

§ 'Naturwiss.,' vol. 14, p. 1203 (1926).

On the other hand the expansion chamber can be made to give the actual range of each particle forming a track, and the evidence in connection with any given track is recorded permanently on a photographic plate. (The plate gives only a two-dimensional picture of tracks in three dimensions, but, as long as all the tracks are approximately in the plane on which the camera is focussed, this need involve no error.) Consequently from a series of photographs we can find the relationship between the range R and the number of particles with ranges between R and $R + \Delta R$ and from this relationship the range of any group of $\alpha$-particles. If the range distribution is Gaussian the mean range will be the same as the most probable range, and it is this, rather than any extrapolated range, which has real meaning for a group of $\alpha$-particles.

In cases where contamination occurs the expansion chamber has a distinct advantage over the scintillation method for in many cases with the expansion chamber tracks due to the presence of contamination can be recognised because they are formed by particles which obviously do not come from the source.

The main objections to the expansion chamber are that in the first place it is recording $\alpha$-particles for no more than 1/5000th of the total life of the source and so many photographs and long periods of photographing are necessary before an accurate value of the range can be obtained, and in the second place there is a little difficulty in finding accurately the stopping power of the gas in the chamber at the moment of admission of the particles.*

## *Experimental Arrangement.*

Within the last year considerable attention has been given to the ranges of the various groups of $\alpha$-particles emitted by radioactive substances, for according to Rutherford's† recent theory certain $\alpha$-particle ranges only are possible. The theory is fairly successful when applied to the ranges of known groups of α-particles and so there is some interest in testing it by examining how closely it predicts the ranges of the long range α-particle groups.

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* For details of previous range measurements with an expansion chamber see Van der Merwe, 'Phil. Mag.,' vol. 45, p. 379 (1923); Curie, 'Ann. Physique,' vol. 3, p. 299 (1925); Curie and Mercier, 'J. Physique,' vol. 7, p. 289 (1926); Meitner and Freitag, *loc. cit.*; Laurence, 'Phil. Mag.,' vol. 5, p. 1027 (1928).

† 'Phil. Mag.,' vol. 4, p. 580 (1927).

The experiments were therefore undertaken with a view to finding accurately the ranges of the α-particle groups which were supposed to exist rather than with the intention of looking for new groups of α-particles, for obviously it is only when dealing with groups which contain comparatively large numbers of α-particles that it is practicable to use the expansion chamber for range measurements.

Despite the conclusion of Meitner and Freitag as to the certainty with which α-particles can be distinguished from swift protons by the density of the tracks they produce, it was felt that only such experimental arrangements should be used as did not furnish an appreciable number of protons within the interval of range in which long range particles were expected. It is almost certain that it is impossible to prepare a source which does not emit a small number of "natural" protons. These particles, which are almost certainly secondary in origin and depend upon the method of preparation of the source, are mostly, perhaps entirely, of very long range, and so there is little lost if the experimental arrangement augments the number of protons of range greater than, say, 15 cm. What is required is an arrangement in which the main α-particle groups produce very few protons of apparent range between 7 cm. and 15 cm. for radium C′ and 8·6 cm. and 15 cm. for thorium C′.

Two entirely different arrangements were used, but before describing either of them some mention should be made of expansion chamber apparatus common to both.

The expansion chamber was a standard 16 cm. diameter chamber of the Wilson type in which the glass cylinder had a height of about 4 cm. The lighting was produced by discharging a battery of Leyden jars (0·03 mfd.) through a single quartz mercury lamp similar to that used by Wilson. The lamp was placed at the back of the chamber and by means of a cylindrical lens the light from it was concentrated in the region where tracks were produced by particles from a source in front of the chamber. Vertically above the chamber was a single camera with a lens of aperture f/4·5 and of 15 cm. focal length. The distance between the top of the chamber and the camera lens was about 50 cm. and so the magnification of the camera was approximately 0·4. All photographs were taken on plates and in order to save plates and to increase the speed of working, a plate was placed in the camera and left there until three photographs had been taken on it. This procedure spoils the photographs slightly but otherwise there is no objection to it.

The expansion chamber apparatus was semi-mechanical, a large number of operations being carried out in correct sequence simply by turning a handle. In all cases it was arranged that between each photograph and the next there was a clearing expansion, for without this good photographs were impossible.

With sources having a γ-ray activity equal to that of about 2 mgm. of radium, photographs could be taken at the rate of about 200 per hour, but with stronger sources than this the rate of photography had to be considerably reduced or the photographs became worthless.* For such strong sources the field across the chamber was about 120 volts per cm., but in general with weaker sources a field strength of 50 volts per cm. was quite sufficient to allow of good photography. By calculation from the observed temperature of the room and the pressure in the chamber when the gas had warmed to room temperature some time after an expansion, it was possible to find the density of the air in the chamber at the moment of track formation and hence the stopping power of the air in the chamber at this time. The formula for obtaining the stopping power in this way is derived below.

The same principles were involved in the measurement of the photographs in both arrangements and a formal treatment of the method used is given in what follows.

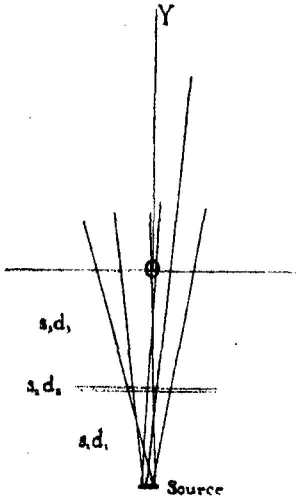

FIG. 1.

Suppose that the magnification of the camera is $\mu$ for points lying in the object plane of the lens and consider a hypothetical photograph showing one long range track and a few tracks belonging to a group of α-particles of known mean range. Suppose that the tracks in the chamber are all in one plane. Fig. 1 shows the positions of the source and the absorbing materials relative to the expansion chamber and also shows the tracks which are to be photographed and the coordinate system by which their lengths are to be found. The source is in a medium (air, oxygen or carbon dioxide) of stopping power (with respect to standard air) $s_1$ and is $d_1$ cm. away from a second medium (mica) of thickness $d_2$ and stopping power $s_2$. Suppose that a given track formed by a member of the group of α-particles of known mean range $R_0$ makes an angle $\theta$ with the axis OY and that its end point has ordinate $y$

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* *Cf.* p. 677.

measured parallel to this axis. Suppose also that the distance between the reference point O and the nearer side of the mica is $d_3$ and that the stopping power of the gas in the chamber is $s_3$. Then the equivalent range in standard air of the particle considered is $[s_1d_1 + s_2d_2 + s_3d_3 + ys_3] \sec \theta$ cm. of standard air. If there are $n$ such tracks belonging to the group of range $R_0$ we can find the mean range for these $n$ tracks and this will be very close to $R_0$ the true mean range.

Therefore

$$nR_0 = \sum_n [s_1d_1 + s_2d_2 + s_3d_3 + ys_3] \sec \theta,$$

or

$$R_0 = [s_1d_1 + s_2d_2 + s_3d_3]\, \overline{\sec \theta} + s_3\, \overline{y \sec \theta}, \qquad (1)$$

where

$$\overline{\sec \theta} \equiv \frac{1}{n} \sum_n \sec \theta \quad \text{and} \quad \overline{y \sec \theta} \equiv \frac{1}{n} \sum_n y \sec \theta.$$

Therefore

$$[s_1d_1 + s_2d_2 + s_3d_3] = (R_0 - s_3\, \overline{y \sec \theta})/\, \overline{\sec \theta}. \qquad (2)$$

Suppose that the long range track makes an angle $\theta_1$ with the $y$ axis and that its end point has ordinate $y_1$.

Then, neglecting the very small change of stopping power with velocity of the particle, R, the range of the particle, is

$$[s_1d_1 + s_2d_2 + s_3d_3] \sec \theta_1 + s_3y_1 \sec \theta_1$$

*i.e.*,

$$R = [R_0 - s_3\overline{y \sec \theta} + y_1s_3\, \overline{\sec \theta}] \sec \theta_1/\, \overline{\sec \theta},$$

$y$ is the actual distance in the chamber, and so if $\eta$ is the variable on the plate corresponding to $y$ in the chamber, we have $\eta = y\mu$ and consequently in terms of distances on the plate

$$R = [R_0\mu - s_3\overline{\eta \sec \theta} + s_3\, \overline{\sec \theta}\, \eta_1] \sec \theta_1/\mu\, \overline{\sec \theta}.$$

In general, $\theta$ was so small that $\sec \theta$ was very insensitive to changes in $\theta$ and thus, if measurements of $\eta$ and $\theta$ are made on the plates, and if $R_0$, $s_3$ and $\mu$ are known, R can be accurately determined. $\mu$ is found by photographing a scale in the chamber and $s_3$ calculated from the readings of a mercury manometer which may be connected to the chamber after the expansion has occurred and the gas in the chamber has attained room temperature again. A consideration of the magnitudes involved shows that any one determination of R should in the experiments described below be accurate to about 0·5 mm.

In actual practice we cannot regularly hope to obtain photographs of long range particles on plates containing only a few tracks of range $R_0$ as has been assumed when considering the theory of the measurements. Consequently the photographs of the few particles of range $R_0$ have to be taken at one time and the photographs of the long range particles at another time. As the values of $s_1$ and $s_3$ and perhaps $d_1$ are not the same in the two cases, small corrections have to be made on account of these changes, but these corrections are so small that R can accurately be found provided that $d_1$ and $d_3$ are approximately known.

In the first arrangement the radioactive material was deposited on a small platinum plate 2·5 mm. long and 0·8 mm. broad. This source, S, (see fig. 2) was put outside the chamber in air and about 7 mm. in front of a mica window, W, 5·2 mm. in diameter. The mica used, chosen for its uniformity, had a stopping power of just over 2 cm. of standard air and closed a small hole drilled through the glass wall of the expansion chamber. Between the source and the mica window was a lead screen, L, with a hole in it, and arrangements were made so that at the correct time this screen could be driven downwards by means of a strong spring. In general, the screen was stopped again as soon as the hole in it was in such a position that the particles could enter the chamber, and a moment later the screen was allowed to fall further so that the particles were cut off again. Inside the chamber was a lead block, B, with a slot in it through which the α-particles passed, but the beam was limited not by this slot but by a horizontal slit 19 mm. long and 2·2 mm. high in a piece of mica attached to the face of the lead block. Fig. 2 shows a vertical section of the arrangement. A calculation, using the fact that the slit on the lead block was 2·3 cm. from the mica window, shows that even particles of 12 cm. range would never be as much as 6 mm. above or below the object plane of the camera, and while the photograph of such a track will not give a true measure of its length, yet with the actual arrangement used the measured range could not differ by more than 0·25 mm. from the true range. As the error may either be positive or negative it must have a negligible effect on the value of a mean range determined from a number of particles.

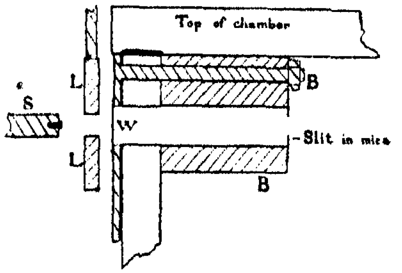

Fig. 2.

In this arrangement swift protons can originate in many ways, for, besides the natural H-particles from the source, secondary H-particles will be produced by disintegration of nitrogen atoms both inside and outside of the chamber, by disintegration of aluminium atoms in the mica, and by the ejection of protons from the water vapour in the air inside and outside the chamber and from the water of constitution of the mica.

The angular spread of the beam (in the horizontal plane only) was about 40°, and so when considering the possibility of recognising protons produced inside the chamber it is reasonable to assume that most of those ejected at an angle greater than 30° with the direction of the impinging α-particle would be recognised as such. As far as disintegration protons are concerned little is known with certainty except that many of them have very long ranges. On investigating the number of secondary H-particles produced from various places, it appears that in all every $10^6$ α-particles of 7 cm. range would produce by elastic collision about 1·5 protons of apparent range between 7 and 15 cm. making an angle of less than 30° with the direction of the incident α-particle, and in addition to these a number of protons from aluminium and nitrogen disintegrations about which little is known.

The arrangement just described was used only with radium C sources. Calibration was effected by waiting until the radium C source had so far decayed in situ that it produced only about 40 tracks per expansion. Four photographs were taken at this stage and these were subsequently measured up to give $\overline{\eta \sec \theta}$ and $\overline{\sec \theta}$.

In general, a spot on the top of the piston was taken as the zero from which to make the measurements, and even though this spot was somewhat out of focus it provided a perfectly reliable zero.

The slit which let in the α-particles had a mechanical oscillograph built into it and it was also possible to connect the piston of the expansion chamber to a second oscillograph mirror on the slit system. By taking oscillograms of an expansion with the timing of the slit the same as that used during a run, it was possible to find the mean position of the piston during the time of entry of the particles.

If $p_0$ is the pressure in the chamber before expansion, and $p_0 - p_1$ the pressure when the air has attained room temperature again after an expansion (the piston is still down), and if $p_w$ is the pressure of water vapour at room temperature then the expansion ratio $v_2/v_1$ is $(p_0 - p_w)/(p_0 - p_1 - p_w)$.* If, however, the piston has completed only $1 - \varepsilon$ of its total travel when the particles enter the chamber then the actual expansion ratio used is $\{v_2 - \varepsilon (v_2 - v_1)\}/v_1$ or $(p_0 - p_w - \varepsilon p_1)/(p_0 - p_1 - p_w)$. Suppose that the air in the chamber is initially at a temperature $t_0$ and that $t_{15}$ and $p_{76}$ are the temperature and pressure of standard air, then the stopping power of the gas in the chamber relative to standard air before an expansion is

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* $v_1$ is initial volume above piston and $v_2$ volume after expansion. The pressure relationship assumes that the air in the chamber has become saturated before $p_0 - p_1$ is measured.

$$\frac{t_{15}}{t_0}\left[\frac{p_0 - p_w}{p_{76}} + \frac{p_w S}{p_{76}}\right],$$

where S is the stopping power (with respect to standard air) of water vapour at standard temperature and pressure. If we assume that during the expansion the mass of water vapour in the chamber is not sensibly altered, we obtain for the mean stopping power of the gas during the time of entry of the particles

$$\frac{p_0 - p_1 - p_w}{p_0 - p_w - \varepsilon p_1}[p_0 - p_w + Sp_w]\,\frac{t_{15}}{t_0 p_{76}}. \qquad (3)$$

The value of $\varepsilon$ was found to depend somewhat on the material on to which the piston fell. With thick rubber it had a value as high as 0·19, with thin rubber it was 0·11, and with leather instead of rubber it was 0·07. For accurate range measurements considerable error results in assuming $\varepsilon = 0$.

The second arrangement was designed to avoid the bulk of the disintegration protons which, as mentioned above, were produced in the first arrangement. For this purpose an entirely new slit system was built in order to make it possible to surround the radioactive source with a gas which did not undergo disintegration. The shutter arrangement was as shown in fig. 3.

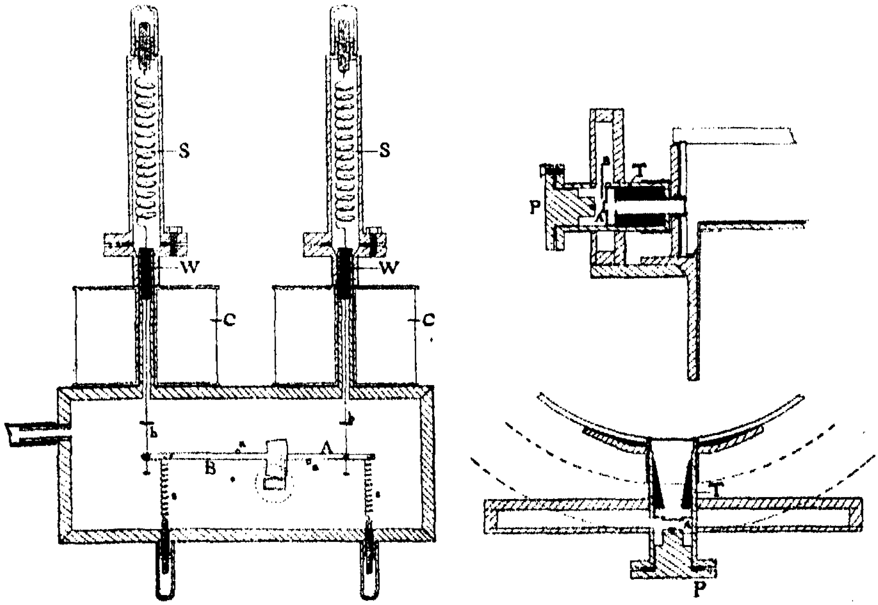

Fig. 3.

When the current flowed through the coils C the iron weights W were pulled downwards and the small springs *s* pulled the levers A and B against the stops *a*. When the currents in the coils were broken, the weights W were pulled upwards by the springs S. After these weights had moved 5 mm., the acceleration being about 10 g., stops on the wires *b* came in contact with the levers and the lever A was turned clockwise and the screen on the left-hand end of it uncovered a slit in a piece of brass, and the lever B was similarly turned clockwise and the screen on the right-hand end of it covered the slit again. The currents in the two coils were broken separately by a high speed switch and it was possible to alter the time between the opening of the two circuits, and so the time for which the slit was uncovered.

As the levers were made extremely light the slit was very quickly opened and closed. The radioactive source was placed immediately behind the screens (to the left in the vertical section of fig. 3) and as mentioned above immediately in front of them was the slit, made double in the form of a box. The end of the tube T (see fig. 3) was closed by a mica window and this whole tube was waxed into the front of the expansion chamber. The mica used was uniform in thickness and had a stopping power between 1 and 1·5 cm. of air. After an expansion the pressure in the box was much higher than that in the chamber, and, as it was necessary to exhaust the box in the process of filling it, the mica was supported between two metal grids to which it was waxed. The effective area of the mica window was 16 × 4 mm., the double grid containing sixteen holes 2 mm. square. Provided the mica was well waxed in, it easily stood a difference of pressure of half an atmosphere in either direction, and doubtless it would have stood more.

This box was at first filled with carbon dioxide at fairly high pressure but it was found that, with such high absorptions in the box, the tracks formed were not as good as those obtained when, say, oxygen at atmospheric pressure was used in the box. It appears that the tracks must be formed at a considerable distance from a strong source or else the strong γ-ray ionisation prevents good track formation.

The source used was a platinum button 2·4 mm. in diameter, which was screwed tightly into the brass plug P closing the back of the tube T. This button was then about 3·6 cm. from the mica window. With the exception of the two short runs when carbon dioxide was used, the box was filled with oxygen at a pressure of about 81 cm. of mercury.

Under these conditions a 12 cm. particle at the end of its track might be as far as 10 mm. from the object plane of the camera lens, but the arrangements were such that particles of this range ended very near to the centre of the chamber and as the axis of the camera lens passed through this point the position of the end of the track on the plate was little influenced by the amount the track was above or below the object plane of the camera.

Two brass pins were fixed at opposite sides of the chamber so as to lie in the mean plane of the entering α-particles and so that the line joining their ends was perpendicular to the direction of the central ray of the α-particle beam. These pins appeared on all the photographs and provided a suitable base line from which to make the measurement of the plates.

In this arrangement the calibration was carried out with a weak source of thorium C, the measurements being made on the 8·6 cm. α-particles. Calibrations were necessary only as often as the mica was changed, for conditions were sufficiently similar from day to day to make only small corrections necessary for changes of density in the chamber and in the box containing oxygen.

The value of the correcting factor ε was assumed the same in this series of experiments as in that for which it was directly measured. The stopping power of the gas in the chamber obtained in this way using equation (3) and measured values of $p_0$, etc., was then compared with a value found directly from experiment. This value was obtained by taking two sets of photographs with the same source, the box being filled with air, first at atmospheric pressure $\pi_0$, and then at some smaller pressure $\pi_1$. Then, by equation (1), for the first series,

$$R_0 = (s_1d_1 + s_2d_2 + s_3d_3)\,\overline{\sec\theta_0} + s_3\overline{y_0\sec\theta_0} \tag{4}$$

and, for the second series,

$$R_0 = \left(s_1d_1\frac{\pi_1}{\pi_0} + s_2d_2 + s_3d_3\right)\overline{\sec\theta_1} + s_3\overline{y_1\sec\theta_1}. \tag{5}$$

Therefore

$$[s_1d_1 + s_2d_2 + s_3d_3]\,\overline{\sec\theta_0} + s_3\overline{y_0\sec\theta_0}$$
$$= \left[s_1d_1\frac{\pi_1}{\pi_0} + s_2d_2 + s_3d_3\right]\overline{\sec\theta_1} + s_3\overline{y_1\sec\theta_1},$$

or

$$s_3\,[\overline{y_0\sec\theta_0} - \overline{y_1\sec\theta_1}] = s_1d_1\left[\frac{\pi_1}{\pi_0}\overline{\sec\theta_1} - \overline{\sec\theta_0}\right]$$
$$+ [s_2d_2 + s_3d_3]\,[\overline{\sec\theta_1} - \overline{\sec\theta_0}]. \tag{6}$$

In general, $\overline{\sec\theta_1}$ is very nearly equal to $\overline{\sec\theta_0}$ and hence only a very approximate value of $s_2d_2 + s_3d_3$ is required; and knowing $s_1d_1$ which was capable of accurate measurement, such a value can be obtained from equation (4) if $R_0$ is known. Hence, from equation (6) above, we can find $s_3$ the actual mean density at the time of entry of the particles. The value obtained using thorium C′ α-particles agreed well with the value calculated from equation (3).

In this arrangement the number of swift protons produced is much smaller than before, and as the width of the beam was only 30° we need consider only the number produced within 20° of the direction of the incident α-particle. Oxygen in the box was equivalent in stopping power to nearly 4 cm. of standard air and so α-particles from radium C′ entering the mica window had a range of 3 cm. only. Thus very few, if any, disintegration protons would be produced from the mica, and consequently, besides natural H-particles from the source, we have only to consider those ejected from the water of constitution of the mica and from the water vapour in the chamber.

On the same basis of calculation as before we find that $10^6$ α-particles produce somewhat fewer than 0·25 proton in passing through the piece of mica (1·5 cm. is assumed as its equivalent thickness) and in the chamber an additional 0·25 proton. The number of protons produced in the chamber does not include those ejected in the last 2 mm. (in standard air) of the path of the particle, because, although very many protons must arise here, their ranges are so short that they do not really affect the measurements. Thus the total number of non-disintegration protons likely to cause confusion has been decreased to about one-third of the number in the previous case and the number of disintegration protons must have been enormously reduced. Calculation shows that considerably more protons are produced when thorium C replaces radium C, but even here the number is only about 1 per $10^6$ 8·6 cm. α-particles and the 4·8 cm. α-particles produce no protons that are seen beyond the 8·6 cm. main beam. In addition, there are so many long range particles emitted from thorium C that the protons produced here are much less serious than in the case of radium C first considered.

In taking a run on radium C a source of radium B + C of about 10 mg. γ-ray activity was obtained by exposing the platinum button to radon. The source was washed in alcohol and then heated to 450° C. in an exhausted silica tube. Eighteen minutes after taking the source off it was placed in position in the box which was then exhausted to a pressure of about 5 mm. Oxygen was blown into the box, it was again exhausted and it was then filled with oxygen to the desired pressure and was left in communication with a bulb of oxygen of about 2 litres capacity. Throughout the run a careful watch was kept on the pressure in this box, on the temperature of the room and on the pressure of the air in the chamber after an expansion. With a radium C source photography was continued for from 2 to 2½ hours.

For measurements on the long range particles from thorium C, sources of thorium B + C were available and so, on account of the long period of thorium B, photography could be continued for 3 hours or more and in all ways runs on thorium B + C could be carried out with much less haste than was imperative in the case of radium B + C. Sources up to 4·3 mg. γ-ray activity were used in the case of thorium C. Separate platinum buttons and plugs were kept for the two types of source.

### *Results.*

Thorium C.—Only the second arrangement was used and most of the data were obtained as the result of two runs using oxygen in the box. Previously, in runs in which carbon dioxide was used in the box, about 70 tracks were photographed and their ranges are included in the results. In all, about 1200 photographs were taken and on these were obtained the tracks of 563 long range particles. Thirteen of these particles passed outside the chamber and nine had ranges between 12·5 and 17 cm. Fig. 4 shows the ranges of all particles lying between 9·0 and 15·0 cm.

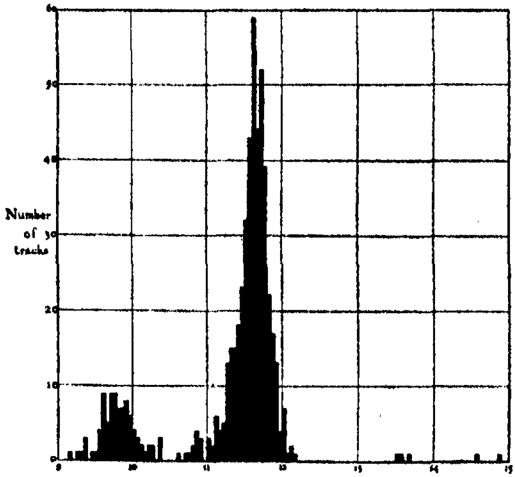

FIG. 4.

It will be seen that these tracks fall into two groups, and if the mean ranges are calculated for these groups they are found to be 9·82 and 11·62 cm. in standard air. As has already been pointed out the method of measurement yields the range of a given α-particle as so much in excess of the mean range of a group of α-particles, and in giving the above values for the mean ranges of these groups from thorium C it is assumed that the mean range of the thorium C′ α-particles is 8·54 cm. The exact value of the mean range is doubtful, but as the difference between extrapolated ionisation ranges is not likely to be very different from that between mean ranges for corresponding groups the extrapolated ionisation ranges of these groups can be taken as 9·90 cm. and 11·70 cm.

The curves in fig. 5 show the distribution* of range of the 11·7 cm. particles photographed and also that of 161 particles of range 8·62 cm. used in the calibration for this series of photographs. One naturally expects that the straggling for the 11·7 cm. particles will be greater than that of the 8·6 cm. particles, both from the theory of straggling and also because of increased artificial straggling produced by the expansion chamber. The fact, however, that the curves are of the same shape and of not very different widths indicates that these 11·7 cm. particles are α-particles ejected from the source with almost constant velocity. The distribution of the 9·9 cm. particles is similar to those of the 8·6 and 11·7 cm. particles, but too few tracks are available to allow a straggling curve to be drawn.

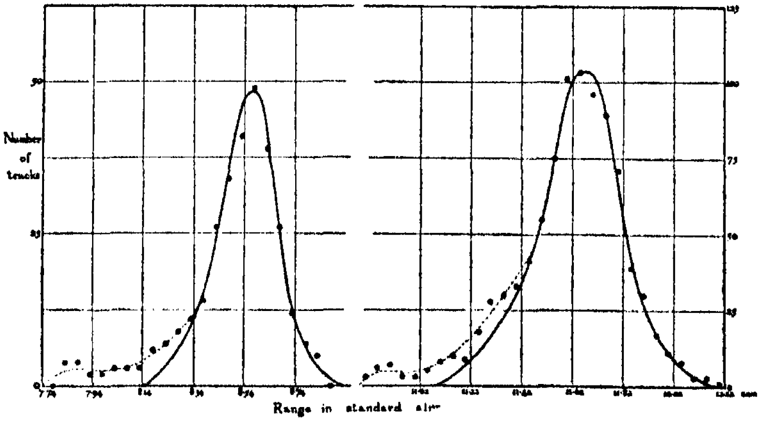

FIG. 5.

Radium C.—Here both arrangements were used. The first arrangement yielded 188 long range tracks and of these 41 passed outside the chamber, the second yielded 273 long range tracks of which 15 only passed outside the chamber. The distribution of length of tracks in these two series is shown in fig. 6 (*a*) and (*b*) where once more the distances represent mean ranges in standard air on the assumption that the mean range for radium C′ α-particles is 6·90 cm. (fig. 6 (*a*) ) and that the mean range for thorium C′ α-particles is 8·54 cm. (fig. 6 (*b*) ). A comparison of the two sets of results indicates that except for the difference in the numbers of long range tracks going right across the chamber* there is nothing essentially different between them and so they were combined to give fig. 6 (*c*).

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* In this case in order to smooth the curve a moving average was taken using each track twice.

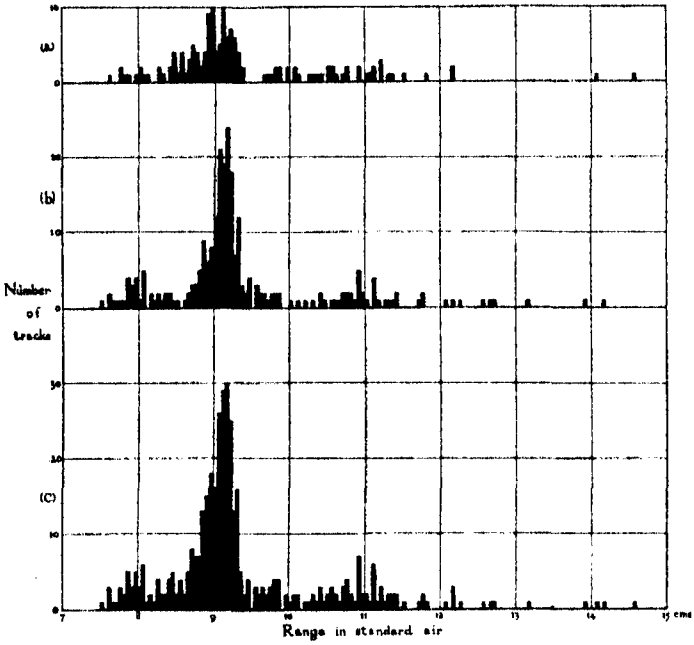

FIG. 6.

From this figure one thing can be deduced with certainty and that is that there is a group of α-particles with a mean range just greater than 9 cm. If one calculates as a first approximation the mean range of all tracks between 8·1 and 10·0 cm. the value obtained is 9·08 cm., and if one then calculates the mean range of those tracks (241) having ranges between 8·6 and 9·5 cm. the value 9·08 cm. is again obtained, and, as the second calculation is likely to include all the tracks in this group, 9·08 may be taken as the mean range of the group and 9·16 cm. as the extrapolated ionisation range. Further consideration of fig. 6 (*c*) is reserved for the discussion which follows. A series of photographs is reproduced and a description of them is included as an appendix to the paper.

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* In the second arrangement these had been reduced to numbers comparable with those to be expected from the results of Rutherford and Chadwick (*loc. cit.*).

### *Discussion.*

There can be little doubt that almost all the tracks photographed are α-particle tracks and not those caused by fast protons. This question has been discussed already and the conclusion reached is supported by the fact that the straggling coefficients of the main groups are of the order to be expected for α-particles emitted by the source with uniform velocity. If, however, one examines the tracks which go to make up these groups, one finds that some of them are very thin and in all respects similar to those formed by protons of high speed. While it may be taken as certain that under given conditions an α-particle will form a denser track than a fast proton, it seems that in the actual use of an expansion chamber variation of the lighting in different parts of the chamber and of the time of entry of the particles may cause such differences in the appearance of the tracks that an α-particle track may be actually or photographically as thin as a proton track formed under good conditions. As a result of our experience in this work we have come to the conclusion that the density of the track formed in an expansion chamber is not always a reliable means for distinguishing between fast protons and α-particles.

A point of some interest is the relative numbers of α-particles in the 9·9 and 11·7 cm. groups from thorium C. The ratio of these numbers has been measured by Meitner and Freitag* using an expansion chamber and again by Philipp† using the scintillation method. The results obtained in both these experiments agree in fixing the ratio at 1 : 2·8. For the same ratio the value obtained here is 1 : 5·1. While the present work has shown that the expansion chamber is not a reliable instrument for counting α-particles, it is surprising that the difference between the results of Meitner and Freitag and those obtained here is so large. It is perhaps worthy of note that Philipp found swift protons to the extent of 18 per cent. of the number of long range α-particles observed, while in the arrangement of Meitner and Feitag they were present to the extent of 11 per cent. of the long range α-particles. In the experiments described here the very long range tracks going across the chamber were less in number than 3 per cent. of the long range α-particle tracks.

In the case of thorium C besides 541 tracks between 8·6 and 12·2 cm. range, 9 tracks were found which did not cross the chamber and which had ranges greater than 12·5 cm. It seems unlikely that many of these tracks can be due to fast protons, and the view taken at present is that these tracks were formed by α-particles ejected by the source. It is quite impossible that they were caused by radioactive contamination.

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* *Loc. cit.*

† *Loc. cit.*

In the case of radium C also the view taken is that the tracks observed with ranges other than 9·2 cm. were formed by α-particles coming from the source. It is impossible to explain the results as being due in part to radioactive contamination, for, though evidence of contamination was sought, it was not found. The results make it quite clear that radium C does not emit only two groups of long range α-particles of 9·3 and 11·3 cm. range as has been supposed for some time on the evidence of scintillation experiments, though the distribution curve shows those particles which in such experiments would produce an effect like an α-particle group of 11·3 cm. range.

When discussing a distribution curve such as fig. 6 (*c*), it is reasonable to postulate that the α-particles forming the tracks observed are emitted in groups of definite velocity, even though it might be possible to explain the distribution by supposing it to be caused, partly or wholly, by a continuous spectrum of α-particles. In the case of the results obtained for radium C the possibility of a continuous spectrum of particles cannot be entirely neglected, but as the chief features of the observed distribution can be explained by assuming groups with ranges of 8·1 and 11·0 cm., with possibly another group at about 10 cm., this explanation is preferable to any which requires a continuous α-ray spectrum. Thus there is strong evidence for additional groups at 8·1 and 11·0 cm. with a doubtful group at about 10 cm. and these groups and the one at 9·2 cm. are considered to include most of the long-range α-particles emitted from radium C, though in addition there are a few particles, most of which must be α-particles from the source, with ranges greater than 12 cm.

It is possible to make a comparison between the results obtained with thorium C and radium C in two slightly different ways. Attention may be directed to the distributions obtained with the same numbers of long range α-particles, or else to the numbers and distributions of the long range particles accompanying the same numbers of primary α-particles (8·6 cm. or 7·0 cm. particles). While the total numbers of the long range tracks recorded here are in the ratio of 5 : 4, they must be associated with about $2 \times 10^6$ 8·6 cm. α-particles in the case of thorium C and $14 \times 10^6$ 7·0 cm. α-particles in the case of radium C. The second method of comparison is useful when secondary effects are known to be present, but, as these effects are absent in the results described here, the first method of comparison is used.

It is seen that in each case the most abundant group is accompanied by a group of particles of lower velocity containing about one-fifth as many particles as in the larger group. Furthermore, the energies of the 7, 8·1 and 9·2 cm. particles from radium C are in the ratios 1 : 1·09 : 1·18 and closely similar ratios 1 : 1·09 : 1·20 hold for the energies of the particles in the groups of 8·6, 9·9 and 11·7 cm. range from thorium C, a fact which suggests that the 11·7 and 9·9 cm. groups of thorium C may correspond to the 9·2 and 8·1 cm. groups from radium C. This comparison can, however, be carried no further, for there is no group in the particles from thorium C which corresponds to the 11 cm. group from radium C.

The agreement between the extrapolated ranges found and those given on Rutherford's* theory is not very satisfactory, for in two† cases out of three the experimental ranges lie midway between two ranges predicted as possible. That these long range particles come from thorium C and radium C or their products has already been shown, but the position in the radioactive series of the substance producing them is uncertain. They have generally been assumed to come from the C′ bodies,‡ but if such long range particles are associated, according to the normal relation, with very short decay periods, they can only occupy this position in the sequence by originating in an isotope of the C′ body, the isotope being formed by an extra β-branch at the parent C body. The long range particles might be emitted by substances formed by branchings at other points, and if this were the case the experimental values would not be expected to agree with those given for the C′ bodies on the basis of Rutherford's theory.

There is also the possibility that these α-particles do not exist in the nucleus with abnormally high energies. They may be α-particles of the ordinary groups which, just prior to ejection, are in some way supplied with extra energy. If one overlooks the difficulty of finding a source of energy to supply about $2 \times 10^6$ electron volts to a thorium C′ α-particle, this explanation of their presence has much to commend it, for it does not require extra branches and yet it explains the high energy of these particles and their comparatively rare occurrence. If this supply of energy were available only for particles ejected in a very short time after the previous (β) disintegration, then the association of long range particles with thorium C′ and radium C′ and their relative abundance with these elements might possibly find explanation. In any case it would appear significant that these particles are found only with thorium C′ and radium C′, the two substances of most rapid disintegration. If the particles do indeed obtain their high energy as has been suggested their energy would not necessarily correspond to that of a definite orbit in the nucleus.

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* *Loc. cit.*

† The ranges of both groups from thorium C.

‡ The only evidence on this point is that long range α-particles from actinium active deposit have not yet been definitely observed. Here the C′ body is present in very small quantity and the particles of range 6·5 cm. are the normal α-particles from this body.

## *Summary.*

The paper describes in detail experiments which have been made to determine the ranges of the long range α-particles from thorium C and radium C. For this purpose an expansion chamber was employed and descriptions are given of the arrangements used and the precautions taken so that the ranges o the particles might be obtained accurately from photographs of the tracks formed.

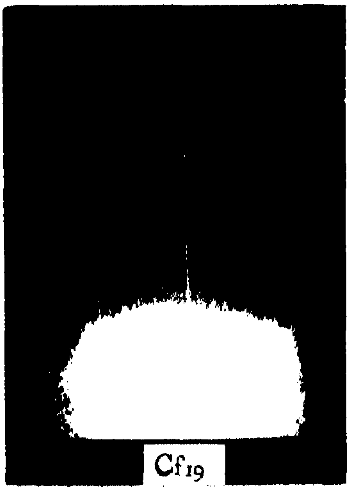
It is concluded that thorium C gives out two groups of α-particles having extrapolated ionisation ranges of 11·70 and 9·90 cm. respectively. A few tracks were found of which the range was greater than 12·5 cm. and these are also thought to be due to α-particles emitted by the source.

In the case of radium C the conclusions are less definite. There is certainly a group of α-particles having an extrapolated ionisation range of 9·16 cm. in standard air, but besides these particles there are other particles with ranges between 7·5 and 12·5 cm. The number of long range tracks available does not allow any absolute decision to be made as to whether these particles are emitted in groups of constant velocity, but there are very strong indications of groups of ranges 8·1 and 11·0 cm. The experiments show without question that radium C does not emit only two groups of α-particles of ranges 9·3 and 11·3 cm. The actual position is much more complex.

We wish to record our thanks to Prof. Sir Ernest Rutherford for the interest that he has taken in these experiments, and for the encouragement which he has given us in what has proved to be a long and trying investigation. Thanks are also due to Dr. Chadwick for much advice and many helpful discussions, and to Dr. Chadwick and Mr. G. R. Crowe for preparing the radioactive sources.

## *Description of Photographs.*

It was the regular practice throughout the work to number all plates before exposure. The serial numbers so assigned have been used for the purpose of the present description. The values of the magnification quoted below are the values of the ratio $\frac{\text{length on photograph}}{\text{length in standard air}}$. The ranges given are ranges in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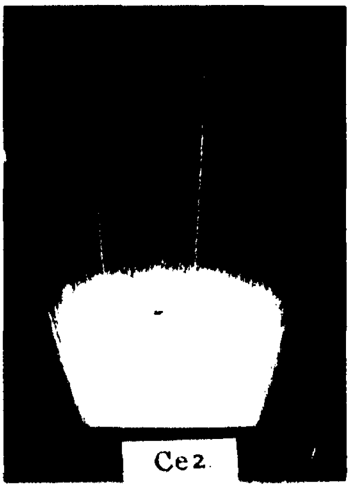
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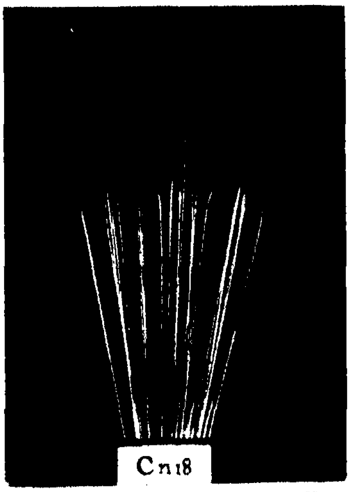
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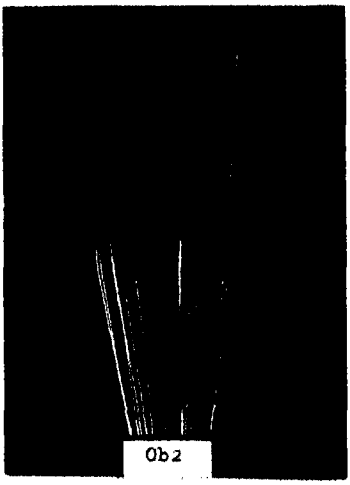
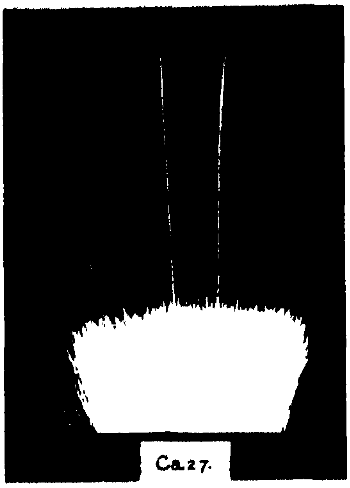
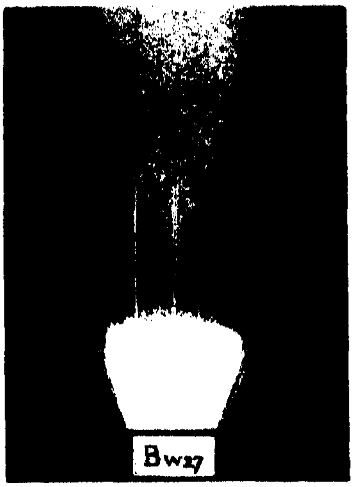
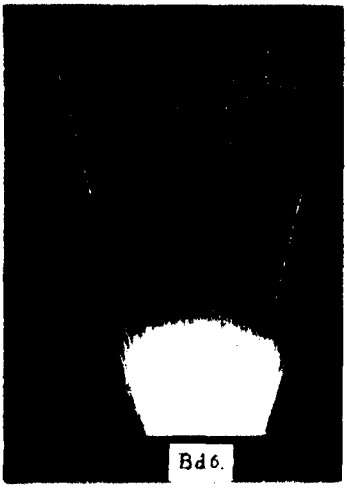

Ob2

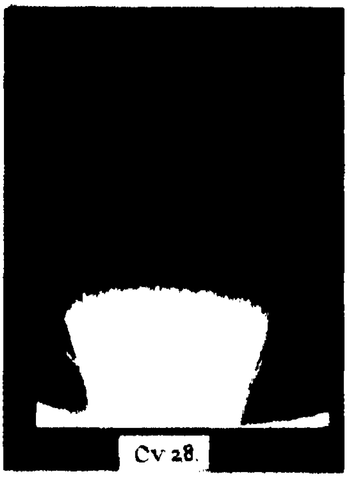

Ca.27.

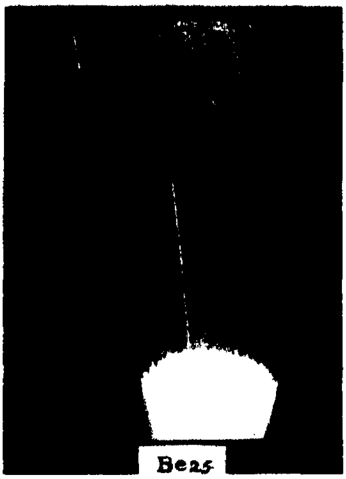

Bw27


Bd 6.

Bn 23.

Bg 4


Cv 28.


Be 25

Df 19.

standard air, and, unless otherwise stated, tracks are taken in order from left to right.

PLATE 11. Long range particles from thorium C.

Cf 19. Magnification 1·03. The right-hand track has range 11·47 cm. Had right-angle photography been employed the left-hand track would have provided very conclusive evidence regarding the nature of the long range particle. With a single photograph no finality is possible, but, owing to the fact that the plane of collision and the object plane of the camera lens cannot be greatly inclined in this case, consideration of the angles on the photograph makes it very unlikely that the collision was other than an α-particle-nitrogen nucleus collision. The very faint track is probably due to a swift proton.

Ce 2. Magnification 1·10. Ranges of long range tracks 9·60, 11·55, 11·52 cm.

Cn 18. Magnification 0·74. Range of long range track 11·40 cm. This photograph and the next were obtained during many test exposures made from time to time with a small source. On plates taken in this way about 3000 8·6 cm. α-particles were registered. On this plate the ends of the 4·8 cm. tracks are also visible.

Ob 2. Magnification 0·91. Range of long range track 11·49 cm.

Ca 27. Magnification 1·15. Ranges of long range tracks 11·59, 11·77, 11·71 cm. This plate was exposed once only.

Bw 27. Magnification 0·65. Ranges of long range tracks 11·64, 11·61, 11·61, 9·92, 14·89 cm.

PLATE 12. Long range particles from radium C.

In this series of photographs special attention is paid to tracks which do not belong to the most abundant group, viz., that at 9·08 cm. mean range. Only one track of that group is included.

Bd 6. Magnification 1·10. Ranges of long range tracks 11·04, 8·93 cm.

Bn 23. Magnification 1·05. Range of long range track 10·91 cm.

Bg 4. Magnification 1·34. Range of long range track 8·42 cm.

Cv 28. Magnification 1·33. Range of long range track 8·36 cm.

Be 25. Magnification 0·94. Ranges of long range tracks 12·17, 9·80 cm.

Df 19. Magnification 1·34. Ranges of long range tracks 10·00, 7·68, 10·42 cm.

# *The Spectrum of* $H_2$: *The Bands Analogous to the Ortho-helium Line Spectrum.*

By O. W. Richardson, Yarrow Research Professor of the Royal Society, and K. Das, King's College, London.

(Received December 19, 1928.)

## § 1. *The α Bands.*

In "Structure in the Secondary Spectrum of Hydrogen—Part V"* it was shown that there existed in this spectrum a very extensive series of bands whose null lines were related by a Rydberg-Ritz formula and whose electronic terms were very close to those of the principal series of the so-called helium doublets (orthohelium) showing that the spectrum of $H_2$ is closely analogous to the line spectrum of He. [It is also very similar to the spectrum of $He_2$.] This similarity has since been confirmed by the discovery and investigation of the absorption spectrum of unexcited $H_2$ by Dieke and Hopfield† from which it appears that none of the final 2 states of that spectrum, in which the transitions are from $1\,^1S$ to an upper 2 state, are the same as the final 2 states of these emission bands. On the other hand their $2\,^1S$ states do agree, to the accuracy of the ultra-violet data, with the final states of an entirely different set of band systems in the visible spectrum which are therefore analogous to the parhelium spectrum.‡

The conclusions of Part V were drawn from a study of the Q branches of the bands only. In an earlier paper§ (Part IV) a preliminary investigation of some of the accompanying P and R branches had been made by a study of the intensity distribution in these bands in the first type discharge. This method enables the lowest rotational quantum number lines of the bands to be picked out with some certainty but the upper lines cannot in general be recognised on account of the faintness of the discharges. These can only be located by finding lines which satisfy some reasonable combination principle. An attempt made by one of us (O.W.R.) in collaboration with Dr. D. B. Deodhar to extend the classification of Part IV led us to the conclusion that the existing data were inadequate, mainly owing to insufficient resolution, to enable a satisfactory decision to be formed as to whether the details of Part IV were correct or ought to be modified.

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* O. W. Richardson, 'Roy. Soc. Proc.,' A, vol. 113, p. 368 (1926).

† 'Phys. Rev.,' vol. 30, p. 401 (1927).

‡ Richardson, 'Roy. Soc. Proc.,' A, vol. 115, p. 528 (1927); Richardson and Davidson, 'Nature,' June 30, 1928.

§ Richardson, 'Roy. Soc. Proc.,' A, vol. 111, p. 714 (1926).

This situation has now been changed owing to the publication of the excellent wave-length tables of Gale, Monk and Lee.* An examination of these fully confirms the very extensive series of systems of Q branches of Part V and the combinations are found to be exact to the accuracy of the new data. This is true in all essential details for the bands which involve the electron transitions $3 \rightarrow 2$ ($\alpha$), $4 \rightarrow 2$ ($\beta$) and $5 \rightarrow 2$ ($\gamma$), but the weak bands involving the $6 \rightarrow 2$ ($\delta$) and higher transitions will require some reconsideration.

By using the more exact new final vibration intervals thus obtained it has been possible to identify with certainty the R and P branches which go with the Q branches of Part V. The new arrangement includes the old lines of Part IV which have the lowest quantum numbers, as it must to harmonise with the microphotometric print of the first type discharge (fig. 2 of that paper), but it abolishes the doublet structure shown in fig. 3 and it appears that there are only 3 branches, P, Q and R, or perhaps it would be better to say P′, Q and R′ as the initial levels for the P′ and R′ branches are different from those for the Q branches. In the R′ branches it appears that there is a final level below any of the final levels present in the Q branches. The corresponding line we call R′(0); it is the same as the R(1) line of Part IV. The new R′(1) line is the same as the old R′(1) line and in fact the new R′(1) branches are, except for one or two of the weaker members, the same as the R branches originally proposed by Dieke.† The new P′(2) lines are the same as the former P (2) lines and the new P′ (3) lines are the same as former Q′ (1) lines in some bands and Q′ (2) lines in others. The new arrangement agrees just as well with the behaviour of the lines in the first type discharge as does the old. These remarks are to be taken as applying only to the axial sequence of bands in the red. The lines which are taken from Fulcher's classification are $R'(0) = S_4$, $R'(1) = S_7$, $P'(3) = S_6$ in the two first bands and $P'(3) = S_5$ in the two others.

Table I shows the lines of the Q branches of the $H_a$ bands using Gale, Monk and Lee's wave-numbers and intensities. The number under *m* indicates the rotational number of the line. The figures such as 2, 0 above each branch indicates that the vibration transition is $2 \rightarrow 0$, etc. A few weak lines not given by Gale, Monk and Lee are included; these are distinguished by the letters M and B (Merton and Barratt), T (Tanaka) and D (Deodhar). The

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* 'Astrophys. J.,' vol. 67, p. 89 (1928).

† 'Proc. K. Akad. Wet., Amsterdam,' vol. 27, p. 490 (1924).

Table I.—

| m | 0, 0 | | 0, 1 | | Mean 1″—0″ | | | Mean 2″—1″ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | From R (0) lines | 2524·32 | | | 2388·26 | | |
| | | | | | | 3·25 | | | 3·14 | |
| 1 | *16611·48 (10) | 2521·08 | 14090·4 (4) | „ Q (1) „ | 2521·07 | | 3·27 | 2385·12 | | 3·18 |
| | | | | | | 6·52 | | | 6·32 | |
| 2 | *16596·87 (10) | 2514·57 | 14081·8 (1) | „ Q (2) „ | 2514·55 | | 3·18 | 2378·80 | | 3·07 |
| | | | | | | 9·70 | | | 9·39 | |
| 3 | *16573·94 (10) | 2504·84 | 14069·1 (0) | „ Q (3) „ | 2504·85 | | 3·18 | 2369·41 | | 2·9 |
| | | | | | | 12·88 | | | 12·35 | |
| 4 | 16544·31 (2) | 2491·91 | 14052·4 (1) | „ Q (4) „ | 2492·00 | | 3·05 | 2357·06 | | 3·08 |
| | | | | | | 15·87 | | | 15·43 | |
| 5 | 16507·71 (2) | | | „ Q (5) „ | 2476·13 | | | 2341·63 | | |
| 6 | 16464·49 (0) | | | | | | | | | |

| m | 1, 0 | | 1, 1 | | 1, 2 | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 18851·66 (9) | 2521·07 | *16330·59 (10) | 2385·09 | 13945·5 (8) | | | | |
| 2 | 18830·58 (5) | 2514·53 | 16316·05 (6) | 2378·85 | 13937·2 (2) | | | | |
| 3 | 18799·23 (5) | 2504·86 | *16294·37 (10) | 2369·37 | 13925·0 (1*a*) | | | | |
| 4 | 18757·83 (1) | 2492·08 | 16265·75 (3) | | | | | | |
| 5 | 18706·54 (1) | 2476·13 | 16230·41 (2) | | | | | | |
| m | 2, 0 | | 2, 1 | | 2, 2 | | 2, 3 | | |
| 1 | 20966·52 (1) | 2521·08 | *18445·44 (10) | 2385·13 | *16060·31 (10) | 2253·01 | 13807·3 (6) | | |
| 2 | 20939·76 (1) | 2514·70 | 18425·06 (8) | 2378·78 | *16046·28 (7) | 2246·88 | 13799·4 (2) | | |
| 3 | 20899·62 (0*a*) | 2504·85 | †18394·77 (10) | 2369·41 | *16025·36 (10) | 2237·76 | 13787·6 (2*a*) | | |
| 4 | | | 18354·75 (2) | 2357·02 | 15997·73 (2) | 2225·63 | 13772·1 (00) | | |
| 5 | | | 18305·25 (2*a*) | 2341·62 | 15963·63 (2) | 2210·43 | 13753·2 (0*b*) | | |
| m | 3, 0 | | 3, 1 | | 3, 2 | | 3, | | 3, 4 |
| 1 | 22960·00 (0) | 2521·11 | 20438·89 (4) | 2385·09 | *18053·80 (10) | 2253·04 | *15800·76 (10) | 2123·76 | 13677·0 (5) |
| 2 | 22927·58 (*p*)<br>(T) | 2514·60 | 20412·98 (1) | 2378·83 | 18034·15 (7) | 2246·92 | *15787·23 (5) | 2117·73 | 13669·5 (1) |
| 3 | | | 20374·29 (1) | 2369·45 | 18004·84 (8) | 2237·74 | *15767·10 (7) | 2108·80 | 13658·3 (1*a*) |
| 4 | | | †20323·15 (5) | 2357·09 | †17960·06 (4) | 2225·57 | 15740·49 (1) | | |
| 5 | | | 20259·51 (1) | 2341·63 | 17917·88 (1) | 2210·35 | 15707·53 (1) | | |
| m | | | 4, 1 | | 4, 2 | | 4, 3 | | 4, 4 |
| 1 | | | 22814·49 (0) | 2385·18 | 19929·31 (1) | 2253·08 | *17676·23 (9) | 2123·86 | *15552·87 (10) |
| 2 | | | | | 19904·16 (0) | 2246·92 | 17657·24 (2) | 2117·86 | 15539·38 (3) |
| 3 | | | | | 19866·70 (1) | 2237·80 | 17628·90 (4) | 2108·85 | *15520·05 (3) |
| 4 | | | | | | | ?17591·22 (4) | 2096·57 | 15494·65 (0)<br>(M. & B.) |
| 5 | | | | | | | 17545·14 (1) | 2082·02 | 15463·12 (0) |
| m | | | | | 5, 2 | | 5, 3 | | 5, 4 |
| 1 | | | | | 21689·41 (0*ah*) | 2253·05 | 19486·36 (3) | 2123·86 | 17312·48 (3) |
| 2 | | | | | | | 19411·89 (0) | 2117·76 | 17294·13 (1) |
| 3 | | | | | | | | | 17266·82 (2) |
| 4 | | | | | | | | | 17230·99(1*ah*) |
| m | | | | | | | 6, 3 | | 6, 4 |
| 1 | | | | | | | 21088·10 (0) | 2123·91 | 18959·19 (3) |
| 2 | | | | | | | 21063·12 (*p*)<br>(T) | 2117·62 | †18935·50 (0) |
| 3 | | | | | | | †21009·39 (2) | 2109·14 | 18900·25 (1*a* ) |
| m | | | | | | | | | 7, 4 |
| 1 | | | | | | | | | ?20493·95 (3) |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | 20419·14 (0) |
| m | | | | | | | | | |
| 1 | | | | | | | | | |
| m | | | | | | | | | |
| 1 | | | | | | | | | |

## $H_a$Q Branches.

| Mean 3″—2″ | | |
|---|---|---|
| 2256·10 | | |
| | 3·05 | |
| 2253·05 | | 3·09 |
| | 6·14 | |
| 2246·91 | | 3·00 |
| | 9·14 | |
| 2237·77 | | 3·03 |
| | 12·17 | |
| 2225·60 | | 3·04 |
| | 15·21 | |
| 2210·39 | | |

| Mean 4″—3″ | | |
|---|---|---|
| 2126·86 | | |
| | 3·01 | |
| 2123·85 | | 3·06 |
| | 6·07 | |
| 2117·78 | | 2·92 |
| | 8·95 | |
| 2108·83 | | 3·31 |
| | 12·26 | |
| *2096·57 | | |

| Mean 5″—4″ | | |
|---|---|---|
| 1996·57 | | |
| | 5·99 | |
| 1990·58 | | 2·84 |
| | 8·83 | |
| 1981·75 | | |

| Mean 6″—5″ | | |
|---|---|---|
| 1869·80 | | |
| | 5·91 | |
| 1863·89 | | 3·02 |
| | 8·93 | |
| 1854·96 | | |

| Mean 7″—6″ |
|---|
| 1742·15 |

| | | | |
|---|---|---|---|
| 2521·07 | | | |
| | 135·95 | | |
| 2385·12 | | 3·88 | |
| | 132·07 | | 1·01 |
| 2253·05 | | 2·87 | |
| | 129·20 | | 0·95 |
| 2123·85 | | 1·92 | |
| | 127·28 | | 1·41 |
| 1996·57 | | 0·52 | |
| | 126·77 | | 1·35 |
| 1869·80 | | +0·84 | |
| | 127·65 | | 1·16 |
| 1742·15 | | +2·00 | |
| | 129·65 | | |
| 1612·5 | | | |

| *m* | Mean 1′—0′ | | |
|---|---|---|---|
| 1 | 2240·21 | | |
| | | 5·98 | |
| 2 | 2234·23 | | 2·97 |
| | | 8·95 | |
| 3 | 2225·28 | | 2·89 |
| | | 11·84 | |
| 4 | 2213·44 | | |

| Mean 2′—1′ | | |
|---|---|---|
| 2114·84 | | |
| | 5·75 | |
| 2109·09 | | 2·96 |
| | 8·71 | |
| 2100·38 | | 2·67 |
| | 11·38 | |
| 2089·00 | | |

| Mean 3′—2′ | | |
|---|---|---|
| 1993·47 | | |
| | 5·61 | |
| 1987·86 | | 2·75 |
| | 8·36 | |
| 1979·50 | | 2·77 |
| | 11·13 | |
| 1968·37 | | 2·96 |
| | 14·09 | |
| 1954·28 | | |

| Mean 4′—3′ | | |
|---|---|---|
| 1875·49 | | |
| | 5·52 | |
| 1869·97 | | 2·55 |
| | 8·17 | |
| 1861·80 | | 2·90 |
| | 11·07 | |
| 1850·73 | | |

| *m* | Mean 5′—4′ | | |
|---|---|---|---|
| 1 | 1760·12 | | |
| | | 5·41 | |
| 2 | 1754·71 | | 2·51 |
| | | 7·92 | |
| 3 | 1746·79 | | 2·53 |
| | | 10·45 | |
| 4 | 1736·34 | | |

| Mean 6′—5′ | | |
|---|---|---|
| 1646·70 | | |
| | 5·25 | |
| 1641·45 | | 2·86 |
| | 8·11 | |
| 1633·34 | | |

| Mean 7′—6′ |
|---|
| 1534·50 |

| | | | |
|---|---|---|---|
| 2240·21 | | | |
| | 125·37 | | |
| 2114·84 | | 4·00 | |
| | 121·37 | | 0·61 |
| 1993·47 | | 3·39 | |
| | 117·98 | | 0·78 |
| 1875·49 | | 2·61 | |
| | 115·37 | | 0·66 |
| 1760·12 | | 1·95 | |
| | 113·42 | | 0·73 |
| 1646·70 | | 1·22 | |
| | 112·20 | | 0·93 |
| 1534·50 | | 0·29 | |
| | 111·91 | | 0·91 |
| 1422·59 | | 0·62 | |
| | 112·53 | | |
| 1310·06 | | | |

| | 4, 5 |
|---|---|
| 1996·57 | 13555·8 (3) |
| 1990·58 | 13548·8 (0) |
| 1981·75 | 13538·3 (1) |

| | 5, 5 | | 5,6 | | 5, 7 |
|---|---|---|---|---|---|
| 1996·57 | *15315·91 (3) | 1869·81 | 13446·1 (1) | 1742·1 (0) | 11704·0 (00) |
| 1990·61 | 15303·52 (1) | 1864·02 | 13439·5 (00) | | |
| 1981·71 | †15285·11 (2) | 1854·91 | 13430·2 (00) | | |

| | 6, 5 | | 6, 6 | | 6, 7 | | 6, 8 |
|---|---|---|---|---|---|---|---|
| 1996·56 | 16962·63 (1) | 1869·79 | 15092·84 (2) | 1742·24 | 13350·6 (1) | 1612·5 | 11738·1 (0*b*) |
| 1990·56 | 16944·94 (0) | 1863·87 | 15081·07 (0*d*) | | | | |
| 1981·79 | 16918·46 (0) | 1855·01 | 15063·45 (0*h*) | 1730·05 | 13333·4 (00) | | |

| | 7, 5 | | 7, 6 | | 7, 7 | | 7, 8 |
|---|---|---|---|---|---|---|---|
| 1996·8 | 18497·14 (3) | 1869·85 | 16627·29 (1) | 1742·14 | 14885·15 (1*a*) | 1611·65 | 13273·5 (00) |
| 1981·83 | 18437·81 (2) | | | | | | |

| | 8, 5 | | 8, 6 | | 8, 7 | | 8, 8 |
|---|---|---|---|---|---|---|---|
| | 19919·73 (00) | 1869·81 | 18049·92 (1) | 1742·16 | 16307·76 (0) | 1611·63 | 14696·13 (0) |

| | 9, 6 | | 9, 7 |
|---|---|---|---|
| | 19359·98 (0) | 1742·18 | 17617·80 (0) |

Table II.—

| m | 0, 0 | | 0, 1 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 0 | *16676·57 (10) | 2524·17 | 14154·4 (2) | | | | | | |
| 1 | *16730·55 (10) | 2521·05 | 14209·5 (2) | | | | | | |
| 2 | †16774·42 (6) | 2514·62 | 14259·8 (0*ah*) | | | | | | |
| 3 | 16809·70 (6) | 2504·84 | 14304·86 (0) | | | | | | |
| 4 | 16836·04 (1) | | | | | | | | |
| 5 | 16853·01 (1) | | | | | | | | |
| 6 | 16860·14 (1) | | | | | | | | |
| 7 | 16856·91 (1*h*) | | | | | | | | |
| m | 1, 0 | | 1, 1 | | 1, 2 | | | | |
| 0 | †18918·02 (9) | 2524·32 | 16393·70 (9) | 2388·30 | 14005·4 (2) | | | | |
| 1 | 18961·78 (10) | 2521·06 | *16440·72 (10) | 2385·12 | 14055·6 (3) | | | | |
| 2 | 18990·67 (2) | 2514·57 | 16476·10 (7) | 2378·80 | 14097·3 (0) | | | | |
| 3 | †(19006·46 (0*a*)) | 2504·79 | (16501·67 (00)) | | | | | | |
| m | 2, 0 | | 2, 1 | | 2, 2 | | 2, 3 | | |
| 0 | 21034·17 (0*a*) | 2524·39 | 18509·78 (8) | 2388·26 | *16121·52 (8) | 2256·12 | 13865·4 (3) | | |
| 1 | 21075·22 (1) | 2521·17 | *18554·05 (10) | 2385·10 | *16168·95 (10) | 2253·05 | 13915·9 (6) | | |
| 2 | 21102·54 (0) | 2514·77 | 18587·77 (5) | 2378·85 | 16208·92 (4) | 2246·82 | 13962·1 (1*a*) | | |
| 3 | †21114·89 (0*h*) | 2504·65 | 18610·24 (4) | 2369·48 | †16240·81 (5) | 2237·71 | 14003·1 (1) | | |
| 4 | | | 18620·86 (0) | 2356·99 | 16263·87 (1) | 2225·67 | 14038·2 (1) | | |
| 5 | | | †18618·94 (0) | 2341·54 | 16277·40 (1) | 2210·60 | 14066·8 (00) | | |
| m | | | | | 3, 2 | | 3, 3 | | 3, 4 |
| 0 | | | | | †18115·94 (8) | 2256·08 | *15859·86 (5) | 2126·86 | 13733·0 (1) |
| 1 | | | | | *18158·55 (10) | 2253·02 | *15905·53 (10) | 2123·93 | 13781·6 (3) |
| 2 | | | | | †18190·12 (8) | 2246·92 | 15943·20 (3) | 2117·80 | 13825·4 (4) |
| 3 | | | | | 18211·64 (0) | 2237·99 | 15973·65 (*rd*²) D | | |

Initial Term Difference (Mean Value) except *.

0′

| | | | |
|---|---|---|---|
| R2 − P2 = 295·330 | | | |
| | 114·555 | | |
| R3 − P3 = 409·885 | | 3·390 | |
| | 111·165 | | 0·875 |
| *R4 − P4 = 521·05 | | 4·265 | |
| | 106·90 | | 0·915 |
| *R5 − P5 = 627·95 | | 5·18 | |
| | 101·72 | | |
| *R6 − P6 = 729·67 | | | |

1′

| | |
|---|---|
| R2 − P2 = 272·160 | |
| | 103·34 |
| *R3 − P3 = 375·50 | |

2′

| | | | |
|---|---|---|---|
| R2 − P2 = 267·705 | | | |
| | 103·015 | | |
| R3 − P3 = 370·720 | | 3·806 | |
| | 99·209 | | 0·738 |
| R4 − P4 = 469·929 | | 4·544 | |
| | 94·665 | | |
| R5 − P5 = 564·594 | | | |

3′

| | |
|---|---|
| R2 − P2 = 254·390 | |
| | 97·40 |
| R3 − P3 = 351·79 | |

## $H_aR'$ Branches.

| m | Mean 1″−0″ | | |
|---|---|---|---|
| 0 | 2524·32 | | |
| | | 3·23 | |
| 1 | 2521·09 | | 3·26 |
| | | 6·49 | |
| 2 | 2514·60 | | 3·29 |
| | | 9·78 | |
| 3 | 2504·82 | | |

| Mean 2″−1″ | | |
|---|---|---|
| 2388·26 | | |
| | 3·15 | |
| 2385·11 | | 3·13 |
| | 6·28 | |
| 2378·83 | | |

| Mean 3″−2″ | | |
|---|---|---|
| 2256·10 | | |
| | 3·07 | |
| 2253·03 | | 3·09 |
| | 6·16 | |
| 2246·87 | | |

| m | Mean 1′−0′ | | |
|---|---|---|---|
| 0 | 2239·45 | | |
| | | 8·22 | |
| 1 | 2231·28 | | 6·73 |
| | | 14·95 | |
| 2 | 2216·28 | | 4·54 |
| | | 19·40 | |
| 3 | 2196·79 | | |

| Mean 2′−1′ | | |
|---|---|---|
| 2116·08 | | |
| | 2·71 | |
| 2113·37 | | −1·06 |
| | 1·65 | |
| 2111·72 | | +1·57 |
| | 3·22 | |
| 2108·50 | | |

| Mean 3′−2′ | | |
|---|---|---|
| 1994·42 | | |
| | 4·80 | |
| 1989·62 | | 3·67 |
| | 8·47 | |
| 1981·15 | | 1·85 |
| | 10·32 | |
| *1970·83 | | |

| | | |
|---|---|---|
| 2231·23 | | |
| | 117·86 | |
| 2113·37 | | 5·89 |
| | 123·75 | |
| 1980·62 | | |

Final Term Difference (Mean Value) except *.

| 0″ | | | |
|---|---|---|---|
| R0 − P2 = 199·499 | | | |
| | 131·273 | | |
| R1 − P3 = 330·772 | | 2·611 | |
| | 128·662 | | 0·842 |
| R2 − P4 = 459·435 | | 3·453 | |
| | 125·209 | | 0·798 |
| *R3 − P5 = 584·643 | | 4·251 | |
| | 120·958 | | |
| *R4 − P6 = 705·601 | | | |

| | | |
|---|---|---|
| 330·77 | | |
| | 16·23 | |
| 314·54 | | 0 51 |
| | 15·72 | |
| 298·82 | | 0·44 |
| | 15·28 | |
| 283·54 | | 0·29 |
| | 14·99 | |
| 268·55 | | |

| 1″ | | | |
|---|---|---|---|
| R0 − P2 = 189·739 | | | |
| | 124·796 | | |
| R1 − P3 = 314·535 | | 2·421 | |
| | 122·375 | | 1·014 |
| R2 − P4 = 436·910 | | 3·435 | |
| | 118·940 | | 0·437 |
| *R3 − P5 = 555·850 | | 3·872 | |
| | 115·068 | | |
| *R4 − P6 = 670·918 | | | |

| 2″ | | | |
|---|---|---|---|
| R0 − P2 = 180·240 | | | |
| | 118·580 | | |
| R1 − P3 = 298·820 | | 2·370 | |
| | 116·210 | | 0·850 |
| R2 − P4 = 415·030 | | 3·220 | |
| | 112·990 | | 0·860 |
| *R3 − P5 = 528·02 | | 4·080 | |
| | 108·91 | | |
| *R4 − P6 = 636·93 | | | |

| 3″ | | | |
|---|---|---|---|
| R0 − P2 = 171·050 | | | |
| | 112·485 | | |
| R1 − P3 = 283·535 | | 2·305 | |
| | 110·180 | | 0·732 |
| R2 − P4 = 393·715 | | 3·037 | |
| | 107·143 | | |
| *R3 − P5 = 500·858 | | | |

| 4″ | | |
|---|---|---|
| *R0 − P2 = 162·015 | | |
| | 106·532 | |
| *R1 − P3 = 268·547 | | 2·345 |
| | 104·187 | |
| *R2 − P4 = 372·734 | | |

Table III.—

| *m* | 0, 0 | | 0, 1 | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 2 | 16479·06 (7) | 2514·56 | 13964·5 (0) | | | | | | |
| 3 | *16399·79†(10) | 2504·79 | 13895·0 (1) | | | | | | |
| 4 | 16314·99 (4) | | | | | | | | |
| 5 | *16225·06 (8) | | | | | | | | |
| 6 | 16130·47 (2) | | | | | | | | |
| 7 | 16031·77 (2a) | | | | | | | | |
| *m* | 1, 0 | | 1, 1 | | 1, 2 | | | | |
| 2 | 18718·52 (4) | 2514·59 | *16203·93 (7) | 2378·73 | 13825·2 (1) | | | | |
| 3 | 18631·03 (7) | 2504·84 | *16126·19 (10) | 2369·39 | 13756·8 (2a) | | | | |
| 4 | 18531·23 (2) | 2492·05 | 16039·18 (5) | 2356·88 | 13682·3 (0c) | | | | |
| 5 | | | | 15946·21 (r) D | | | | | |
| *m* | | | 2, 1 | | 2, 2 | | 2, 3 | | |
| 2 | | | 18320·06 (6) | 2378·84 | *15941·22 (5) | 2246·92 | 13694·3 (0a) | | |
| 3 | 20744·45 (00a) | 2504·94 | *18239·51 (10) | 2369·41 | *15870·10 (10) | 2237·70 | 13632·4 (2) | | |
| 4 | | | 18150·87 (3) | 2356·98 | 15793·89 (5) | 2225·49 | 13568·4 (0a) | | |
| 5 | 20530·48 (4) | 2476·09 | 18054·39 (8) | 2341·60 | *15712·79 (6) | 2210·59 | 13502·2 (00) | | |
| 6 | | | 17949·95 (2) | 2323·01 | 15626·94 (1) | | | | |
| *m* | | | 3, 1 | | 3, 2 | | 3, 3 | | 3, 4 |
| 2 | | | 20314·59 (2) | 2378·86 | 17935·73 (6) | 2246·92 | *15688·81 (5) | 2117·81 | 13571·0 (0a) |
| 3 | | | 20229·13 (2) | 2369·39 | *17859·74 (10) | 2237·78 | *†15621·96 (10) | 2108·86 | 13513·1 (1) |
| 4 | | | | | 17775·06 (4) | 2225·59 | 15549·47 (3) | 2096·77 | 13452·7 (1) |
| 5 | | | | | | | 15473·43 (rd*) D | | |

lines measured on the interferometer are indicated * and for those marked † there are grounds for believing that they may still be blends. The lines are in alternate columns separated by the corresponding final vibration differences. These will be seen to show an excellent agreement, the extreme variation rarely exceeding 0·1 wave-number if we keep to the lines measured by Gale, Monk and Lee. The table has undergone considerable extension in the region of high vibration numbers since Part V was written. It is also very gratifying that the bad agreement given by the older infra-red data has entirely disappeared. The existence of all the states both initial and final with vibration numbers between 0 and 7 is now securely established and there is some

$H_aP'$ Branches,

| $m$ | Mean $1''-0''$ | | |
|---|---|---|---|
| 2 | 2514·58 | | |
| | | 9·76 | |
| 3 | 2504·82 | | |
| 4 | | | |

| $m$ | Mean $2''-1''$ | | |
|---|---|---|---|
| 2 | 2378·81 | | |
| | | 9·41 | |
| 3 | 2369·40 | | 3·06 |
| | | 12·47 | |
| 4 | 2356·93 | | |

| $m$ | Mean $3''-0''$ | | |
|---|---|---|---|
| 2 | 2246·92 | | |
| | | 9·18 | |
| 3 | 2237·74 | | 3·03 |
| | | 12·21 | |
| 4 | 2225·53 | | |

| $m$ | Mean $1'-0'$ | | |
|---|---|---|---|
| 2 | 2239·45 | | |
| | | 8·23 | |
| 3 | 2231·22 | | 6·76 |
| | | 14·99 | |
| 4 | *2216·23 | | |

| $m$ | Mean $2'-1'$ | | | |
|---|---|---|---|---|
| 2 | 2116·08 | | | |
| | | 2·77 | | |
| 3 | 2113·31 | | 1·10 | |
| | | 1·67 | | 2·89 |
| 4 | 2111·64 | | −1·79 | |
| | | 3·46 | | |
| | *2108·18 | | | |

| $m$ | Mean $3'-2'$ | | | |
|---|---|---|---|---|
| 2 | 1994·51 | | | |
| | | 4·91 | | |
| 3 | 1989·60 | | 3·57 | |
| | | 8·48 | | 2·16 |
| 4 | 1981·12 | | 1·41 | |
| | | 9·89 | | |
| | *1971·23 | | | |

| | | |
|---|---|---|
| 2239·45 | | |
| | 123·33 | |
| 2116·13 | | 1·71 |
| | 121·62 | |
| 1994·51 | | |

---

evidence for the occurrence of $n' = 8$ and 9 and $n'' = 8$. The tables of final and initial vibration differences together with the first and second differences of these quantities with $m$ shown on the right of the diagonal line in Table I shows that the behaviour of all these quantities is very regular. The third differences with $n'$ or $n''$ of the $m = 1$ vibration differences are constant both for initial and final terms. This shows that the usual expression for the vibrational energy which includes only terms as high as $n^2$ is inadequate but that the function can be completely expressed by adding terms in $n^3$ and $n^4$. Conversely this regularity is a high tribute to the accuracy of Gale, Monk and Lee's measurements; in forming the differences the wave-numbers have been recalculated as the wave-lengths are frequently more accurate than the wave-numbers given in the tables.

Tables II and III give similar data for the R′ and P′ branches respectively. As in the Q branches there is in both cases a pronounced alternation in intensity in the lines corresponding to a weight ratio of 3 to 1 for successive rotational states.* This is fairly evident from the eye estimates of intensities given by Gale, Monk and Lee but it is much more evident if the unpublished intensity measures of Kapuscinski and Eymers† are used. For example, their values of the intensities of the first three lines of the various branches of the 0 → 0 band are :—Q (1) = 173·0, Q (2) = 47·0, Q (3) = 81·1, R′ (0) = 40·0, R′ (1) = 120·0, R′ (2) = 34·7, P′ (2) = 24·4, P′ (3) = 67·0, and P′ (4) = 29·5. Throughout the band system the Q branches are stronger than the R′ and the R′ than the P′. This also is exemplified by the foregoing values of the intensities and is true throughout the band system. In each case the maximum strength is close to the symmetrical diagonal progression which is in approximate agreement with Condon's‡ theory of intensity distribution in band systems for systems having constants of this type.

There is a definite perturbation in the $1' \rightarrow n''$ progression, the lines P′ (4) and R′ (2) being either absent or very weak and in any event not in the normal place. This means that the fourth upper rotational level is either absent or is weak and has an abnormal value in the $n' = 1$ vibrational state of the upper electronic level. We have not been able to find any evidence of any initial level with $n' > 3$. Both P′ and R′ branches seem to die out suddenly at the $n' = 4$ progression. This does not conflict with the existence of $n' = 4$, 5, 6, 7 and possibly 8 and 9 in the Q branches because the respective initial levels are not the same. They are also slightly higher for P′ and R′ than they are for Q.

## § 2. *The β Bands.*

Table IV shows the Q branches of the $H_\beta$ band system, electronic transition 4 → 2. The numerous inaccurate or missing lines present in the corresponding tables of Part V have now quite disappeared and some additions have been made in the bands arising from higher vibrational states. The existence of the levels up to $n' = 5$ and $n'' = 5$ is now certain, the inclusion of the few lines which belong to the 6th and 7th levels is perhaps questionable. Table V exhibits what we have been able to find of the R′ and P′ branches for this electron transition. They are extremely weak except the 0 → 0 bands. Such as they are, however, they, as well as the Q branches, have very similar properties to those of the corresponding $H_a$ bands. In each case what strength there is lies on or close to the diagonal sequence. There is the same alternation of intensity in the lines. Kapuscinski and Eymers' intensities of the 0 → 0 lines are Q (1) = 111, Q (2) = 36·5, Q (3) = 53·8, R′ (0) = 21·6, R′ (1) = 76·9, R′ (2) not measured, P′ (2) = 9·6, P′ (3) = 48·4 and P′ (4) = 9·5. P′ (3) either seems too high or P′ (2) and P′ (4) too low. As in the $H_a$ bands the Q branches are the strongest and the P′ branches the weakest. In view of the weakness of the R′ and P′ branches for the 4 → 2 electron transition these branches will be very weak for the higher transitions, if they exist. So far, a rather desultory search for them has not yielded any evidence of their existence.

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* *Cf.* Richardson, 'Roy. Soc. Proc.,' A, vol. 116, p. 484 (1927).

† Since published in 'Roy. Soc. Proc.,' A, vol. 122, p. 58 (1929).

‡ 'Phys. Rev.,' vol. 28, p. 1182 (1926). We intend to return to this in a later communication.

### § 3. *The Rotational Structure of the Bands.*

Having found the R′ and P′ branches we are now able to extend the analysis of Part V to include the rotational structure of these band systems. The general scheme of the levels and the transitions which occur are shown in fig. 1. Since $R'(m) - Q(m) \neq Q(m+1) - P'(m+1)$ the upper levels are double

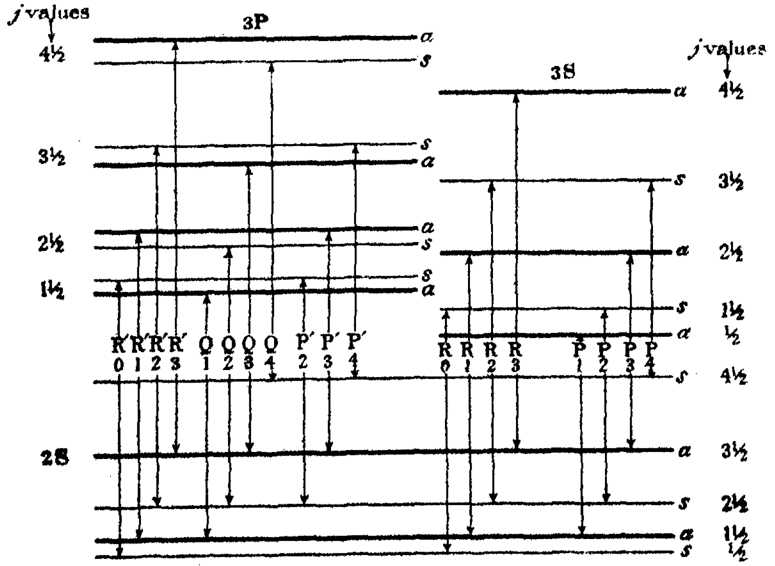

FIG. 1.

**Table IV.—**

| *m* | 0, 0 | | 0, 1 | | | | |
|---|---|---|---|---|---|---|---|
| 1 | *22263·25 (9) | 2521·03 | 19742·22 (6) | | | | |
| 2 | †22247·21 (5) | 2514·52 | 19732·69 (0) | | | | |
| 3 | 22223·30 (4) | 2504·86 | 19718·44 (0) | | | | |
| 4 | 22191·78 (1) | | | | | | |
| *m* | 1, 0 | | 1, 1 | | 1, 2 | | |
| 1 | 24472·87 (2) | 2521·07 | *21951·80 (10) | 2385·04 | 19566·76 (4) | | |
| 2 | 24450·86 (1) | 2514·72 | 21936·14 (5) | 2378·75 | 19557·39 (1) | | |
| 3 | †24417·87 (1) | 2504·85 | 21913·02 (4) | 2369·43 | 19543·59 (2*h*) | | |
| 4 | | | 21882·35 (1*a*) | 2357·02 | 19525·33 (0*a*) | | |
| *m* | 2, 0 | | 2, 1 | | 2, 2 | | 2, 3 |
| 1 | 26556·90 (00) | 2521·16 | 24035·74 (5) | 2385·18 | 21650·56 (10) | 2253·06 | 19397·50 (6) |
| 2 | †26528·79 (*rd*) | 2514·47 | 24014·32 (1) | 2378·88 | 21635·44 (5) | 2246·93 | 19388·51 (1*h*) |
| 3 | | | †23982·37 (2) | 2369·41 | †21612·96 (3) | 2237·87 | 19375·09 (2) |
| 4 | | | | | †21583·62 (9) | 2225·67 | †19357·95 (0*a*) |
| *m* | | | 3, 1 | | 3, 2 | | 3, 3 |
| 1 | | | 25997·76 (0*h*) | 2385·05 | 23612·71 (3) | 2253·12 | 21359·59 (5) |
| 2 | | | | | †23591·95 (1) | 2246·99 | 21344·96 (1) |
| 3 | | | | | 23560·92 (1) | 2237·82 | 21323·11 (2) |
| *m* | | | | | 4, 2 | | 4, 3 |
| 1 | | | given erroneously as 52455·81 by G., M. and L. | | 25455·97 (0) | 2253·24 | 23202·73 (2) |
| 2 | | | | | | | 23182·43 (0) |
| 3 | | | | | | | 23152·36 (1) |
| 4 | | | | | | | |
| *m* | | | | | | | 5, 3 |
| 1 | | | | | | | 24930·56 (0) |
| 2 | | | | | | | 24904·71 (0) |
| 3 | | | | | | | 24866·45 (00) |
| 4 | | | | | | | |
| *m* | | | | | | | |
| 1 | | | | | | | |

## $H_\beta Q$ Branches.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 3, 4 | | | | | | | |
| 2123·85 | 19235·74 (4) | | | | | | | |
| | 19227·90 (1*h*) | | | | | | | |
| 2108·85 | 19214·26 (1) | | | | | | | |
| | 4, 4 | | 4, 5 | | | | | |
| 2123·92 | †21078·81 (6) | 1996·54 | 19082·27 (4) | | | | | |
| 2117·83 | 21064·65 (1) | 1990·67 | 19073·98 (1) | | | | | |
| 2108·83 | 21043·53 (1) | 1981·72 | 19061·81 (1) | | | | | |
| | 21013·94 (1) | 1970·56 | †19043·38 (1) | | | | | |
| | 5, 4 | | 5, 5 | | 5, 6 | | | |
| 2124·09 | 22806·47 (2) | 1996·56 | 20809·91 (2) | 1869·79 | 18940·12 (2) | given erroneously as 18939·77 by G., M. and L. | | |
| 2117·96 | 22786·75 (1) | | †20795·78 (2) | | †18932·31 (0*h*) | | | |
| 2108·76 | 22757·69 (1) | 1981·82 | 20775·87 (0) | | | | | |
| | 22715·27 (0) | 1970·63 | †20744·64 (00*a*) | | | | | |
| | 6, 4 | | 6, 5 | | 6, 6 | | | 6, 7 |
| | 24420·29 (0) | 1996·46 | 22423·83 (1) | 1869·84 | [20553·99] | | 1742·26 | 18811·73 (2) |

Table

## $H_\beta R'$ Branches.

| *m* | 0, 0 | | 0, 1 |
|---|---|---|---|
| 0 | 22329·79 (5) | 2524·35 | †19805·44 (0*a*) |
| 1 | 22379·40 (3) | 2521·01 | †19858·39 (1) |
| 2 | 22419·69 (2) | | |
| 3 | 22449·73 (3) | | |
| 4 | | | |

| *m* | 1, 1 |
|---|---|
| 1 | †22063·07 (3) |
| 2 | 22105·74 (1) |
| 3 | 22139·45 (3) |

| *m* | 2, 2 |
|---|---|
| 1 | 21751·56 (0*h*) |

| *m* | 3, 3 | | 3, 4 |
|---|---|---|---|
| 1 | †21446·79 (3) | 2123·94 | 19322·85 (1) |
| 2 | 21490·50 (0*a*) | | |

**Final Term Difference.**

0''
R0 — P2 = 199·49
R1 — P3 = 330·74
R2 — P4 = 459·51
R3 — P5 = 584·71

1''
R1 — P3 = 314·38
R2 — P4 = 436·92
R3 — P5 = 555·8

2''
R1 — P3 = 298·78

3''
R1 — P3 = 283·47
R2 — P4 = 393·58

**Initial Term Difference.**

0'
$\left.\begin{array}{l}\text{R2 — P2 = 289·39}\\ \text{R3 — P3 = 401·12}\end{array}\right\rangle 121·73$

1'
R2 — P2
R3 — P3 = 390·76

**V.**

## $\mathrm{H}_\beta\mathrm{P}'$ Branches.

| *m* | 0, 0 | 0, 1 |
|---|---|---|
| 2 | 22130·30 (3) | |
| 3 | 22048·66 (7) | 19548·59 (2*h*) |
| 4 | 21960·18 (2) | |
| 5 | 21865·07 (2) | |

| *m* | 1, 1 | | 1, 2 | |
|---|---|---|---|---|
| 2 | | | | |
| 3 | 21748·69 (0*a*) | | | |
| 4 | 21668·82 (0) | 2357·11 | 19311·71 (00) | given erroneously as 19311·20 by G., M. and L. |
| 5 | ††21583·62 (9) | | | |

| *m* | 2, 2 |
|---|---|
| 2 | |
| 3 | †21452·78 (1) |
| 4 | |

| *m* | 3, 3 |
|---|---|
| 2 | |
| 3 | †21163·32 (1) |
| 4 | †21096·92 (1) |

(in most cases $R'(m) - Q(m)$ is $> Q(m+1) - P(m+1)$ ). Since $R(m) - P(m+2)$ has the same value for all bands with the same final level, for a given $m$, it follows that the P′ and R′ transitions arise from the same set of upper levels and the Q branches from a different set. The lower levels on the other hand are single. In each set the weights of alternate levels oscillate in the ratio 3 to 1. In the final states the lowest has weight 1 the second 3, the third 1, the fourth 3, and so on. In the initial states from which the Q lines spring the lowest state has weight 3, the next 1, and so on. In the upper states from which the R′ and P′ lines spring this is reversed, the lowest being weak, the second strong, and so on. The strong levels are denoted by $a$ (antisymmetric) and the weak levels by $s$ (symmetric) in fig. 1. The electronic terms of these bands and the fact that the final states do not occur in the absorption spectrum of $H_2$ leads us to expect that the final states are $2\,{}^3S$ states, and the initial states $2\,{}^3P$ states. If these states are triple the separation of the components must be exceedingly small. Merton and Barratt measured the width of some of the lines and found it to be normal for a molecular weight of 2, and a very large number of them have been measured on the interferometer by Gale, Monk and Lee, who say nothing about any evidence of fine structure. Some suggestion of evidence that there may be something of the sort may be based on the fact that there does seem to be a tendency for the final vibration differences to run very slightly higher for larger values of $n'$. If this is real it is in any event a very small effect. The final vibration and rotation terms which are derived from pairs of lines each measured on the interferometer show the following comparisons :—

$$2_1 1\,P'(3) - 2_1 2\,P'(3) = 2369\cdot419_1, \qquad 2_1 1\,Q(3) - 2_1 2\,Q(3) = 2369\cdot411_0,$$
$$2_1 1\,R'(1) - 2_1 2\,R'(1) = 2385\cdot100_7, \qquad 2_1 1\,Q(1) - 2_1 2\,Q(1) = 2385\cdot119_2,$$
$$3_1 2\,R'(1) - 3_1 3\,R'(1) = 2253\cdot031_4, \qquad 3_1 2\,Q(1) - 3_1 3\,Q(1) = 2253\cdot035_7,$$
$$1_1 1\,R'(1) - 1_1 1\,P'(3) = 314\cdot548_6, \qquad 2_1 1\,R'(1) - 2_1 1\,P'(3) = 314\cdot528_2,$$
$$2_1 2\,R'(1) - 2_1 2\,P'(3) = 298\cdot846_6 \text{ and } 3_1 2\,R'(1) - 3_1 2\,P'(3) = 298\cdot812_6.$$

The agreement of some of these pairs is perhaps not so good as might be expected if the lines had no structure; but when the possibility of the measurements having been affected by the presence of faint blends is borne in mind the existing data hardly seem numerous enough to reach a definite conclusion from.

In any event it is clear that apart from the possibility of some very fine structure the lines of these bands are single. Nevertheless we shall use the symbols $2\,{}^3S$ and $m\,{}^3P$ to represent the electronic states with which they are concerned as this recalls the connection with the principal series of helium "doublets" already referred to and it is desirable to retain the symbol $2\,^1S$ for the states in the new "violet" bands which are common to the 2 states of the ultra-violet absorption spectrum.

Since the number of electrons in the hydrogen molecule is even, if the lower states in fig. 1 are S states they will, according to Mulliken,[*] have the $j$ values $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, etc., and also $\sigma = 0$ and $\rho = 0$; whilst if the upper states are P states the successive $j$ values are $1\frac{1}{2}$, $2\frac{1}{2}$, $3\frac{1}{2}$, etc., and $\sigma = 1$ and $\rho = 0$. It has been pointed out[†] that there is evidence that in this spectrum there are no transitions between symmetric and antisymmetric states, *i.e.*, that all transitions which occur are either antisymmetric → antisymmetric or symmetric → symmetric. We shall adopt this as a guiding principle. In addition we have the usual restriction of the changes of $j$, viz., $\Delta j = 0$ or $\pm 1$. These 2 principles account completely for all the lines which are found, the distribution of intensity among them and the lines which are missing, when the aforementioned $j$ values are adopted. There does not seem to be any need to labour this point. It is obvious from fig. 1 which shows on the left-hand side all the possible lines on this scheme up to R′ (3), Q (4) and P′ (4). The first lines of each branch are respectively R′ (0), Q (1) and P′ (2). The lines Q (0) and P′ (1) are not found because they would have to come from a non-existent upper level. The strong lines are in all cases those which have odd $m$ values, *i.e.*, R′ (1), R′ (3), Q (1), Q (3), P′ (3), P′ (5), etc., and the weak lines those which have even $m$ values, *i.e.*, R′ (0), R′ (2), Q (2), Q (4), P (2), P (4), etc., as is required by the figure when the 3 to 1 ratio of the weights of the antisymmetric to the symmetric states is borne in mind.

We think this proof is conclusive that these bands are $2S - mP$ but we shall offer still further proof that the lower state is a 2S state in a later section of the paper.

We turn now to the numerical values of the rotational band constants. The final rotational term differences are given by

$$R'(m) - P'(m+2) = F''(m+2) - F''(m) \qquad (1)$$

and a brief examination showed that the terms were well represented by expressions of the form

$$F_n''(m) = B_n''(m - \epsilon_n'')^2 + \beta_n''(m - \epsilon_n'')^4, \qquad (2)$$

---

[*] 'Phys. Rev.,' vol. 28, p. 1202 (1926).

[†] Richardson, 'Roy. Soc. Proc.,' A, vol. 116, p. 484 (1927).

*m* being the current number of the line such as for example R (0) as indicated in fig. 1 and $B_n''$ $\beta_n''$ and $\varepsilon_n''$ being taken as constants, the index *n* indicating the vibration number of the final states. In general we used the values of R′ (1) − P′ (3), R′ (2) − P′ (4) and R′ (3) − P′ (5) to determine the 3 constants, we then calculated the values of F″ (0), F″ (1), . . ., F″ (7) and tested the results by comparing the calculated with the observed values of the remaining terms such as F″ (2) − F″ (0), F″ (6) − F″ (4), etc. These agreed to within the accuracy of the data. In making these computations all the wave-number data were recalculated from Gale, Monk and Lee's wave-lengths to 3 decimal places. In most cases the first three term differences are reliable to within 0·01 wave-number (about 1 part in 30,000). In this way we obtained the constants given in the following table.

Table VI.—Constants of the Final Levels.

| $\xrightarrow{}$ Vibrational level $n''$ | 0. | 1. | 2. | 3. | 4. |
|---|---|---|---|---|---|
| $B_n''$ | $33 \cdot 328_{35}$ | $31 \cdot 746_{25}$ | $30 \cdot 148_5$ | $28 \cdot 558_{65}$ | |
| $-\varepsilon_n''$ | 0·503589 | 0·500297 | 0·501228 | 0·505021 | |
| $\beta_n''$ | 0·020532 | 0·020403 | 0·019338 | 0·017953 | |

It will be seen that $\varepsilon_n''$ is very close to $-\frac{1}{2}$ in all cases. As a matter of fact practically as good a fit with the observed data can be got by assuming $\varepsilon = -\frac{1}{2}$ exactly, which is equivalent to the very simple assumption

$$F_n''(m) = B_n''(m+\tfrac{1}{2})^2 + \beta_n''(m+\tfrac{1}{2})^4 \equiv B_n''j^2 + \beta_n''j^4. \qquad (3)$$

For the $n'' = 0$ state the successive term differences are given in the second row of Table VII. The values of these are equal to 3, 5, 7, etc., times the quantities in the third row. From any successive pair of these a value of $\beta_0''$ can be deduced. These values are given in the fourth row. These show a systematic variation with *m* so that β is not constant but if we neglect this and take the average the mean value of β is −0·02100. Taking this value of $\beta_0''$ the data in the second row lead to the values of $2B_0''$ given in the fifth row. The mean of these is $2B_0'' = 66 \cdot 7704$. However, most weight should be attached to the values got from the lower term numbers as these are less affected by the uncertainty in the small quantity $\beta_0''$. On this interpretation ($\varepsilon_0'' = -\frac{1}{2}$), it looks safe to put $2B_0'' = 66 \cdot 773 \pm 0 \cdot 001$. If $\varepsilon_0''$ is not assumed $= -\frac{1}{2}$ the value of $2B_0''$ comes out lower by about 1 part in 500 (Table VI). The value

Table VII.

| $F''(2)-F''(0)$ | $F''(3)-F''(1)$ | $F''(4)-F''(2)$ | $F''(5)-F''(3)$ | $F''(6)-F''(4)$ | $F''(7)-F''(5)$ |
|---|---|---|---|---|---|
| 199·499 | 330·772 | 459·434 | 584·643 | 705·601 | 821·226 |
| $2B_0''+13\beta_0''$ | $2B_0''+29\beta_0''$ | $2B_0''+53\beta_0''$ | $2B_0''+85\beta_0''$ | $2B_0''+125\beta_0''$ | $2B_0''+173\beta_0''$ |
| $\beta_0''$ = −0·02158 | −0·02171 | −0·02103 | −0·02037 | −0·02030 | |
| $2B_0''$ = 66·7727 | 66·7734 | 66·7464 | 66·7553 | 66·7705 | 66·8042 |

| $F''(0)$ | $F''(1)$ | $F''(2)$ | $F''(3)$ | $F''(4)$ | $F''(5)$ | $F''(6)$ | $F''(7)$ |
|---|---|---|---|---|---|---|---|
| 8·345 | 75·011 | 207·838 | 405·818 | 667·439 | 990·686 | 1373·039 | 1811·472 |

of the moment of inertia $I_0''$ of this molecule ($2\,^3S$) corresponding to the above value of $2B_0''$ is $8\cdot2951_4 \times 10^{-41}$ grm. cm.$^2$.

The value $2B_0'' = 66\cdot773 \pm 0\cdot001$ compares with the following previous estimates :—(1) 67·98 in Part V, p. 411. This estimate was based on the arrangement of the P and R branches in Part IV and was got from the wave-numbers of the lowest P line and the two lowest R lines. The reason for the good agreement is that the lowest R and P line respectively are the same as R′ (0) and P′ (2) of the present arrangement and the next R line was very close to R′ (1). (2) 57·4 in Part V by the indirect method depending on the analysis of the vibration rotation cross term applied to the data given by the Q branches. This method only gives rough values and the agreement is of the kind to be anticipated. (3) 60·88 in 'Roy. Soc. Proc.,' A, vol. 114, p. 649 (1927) by the method involving the application of the $m^4$ power term to the Q branch data. This method is also rough, with the data then available. However, it will be seen that none of the old values were very wide of the mark.

Another check on the value of $2B_0''$ can be got by calculating the coefficient $\beta_0''$ of the $m^4$ term. According to Kratzer's theory of the anharmonic oscillator the relation between these constants is given by

$$\beta_0'' = B_0'' \, (2B_0''c/w_0)^2 \qquad (4)$$

Using the present data got from the R′ (0) lines the recalculated values of $w_0$ and $w_0x$ are $w_0 = 2593\cdot06_5$ and $w_0x = 67\cdot99$ compared with the values $w_0 = 2593\cdot82$ and $w_0x = 68\cdot41$ given in Part V. On substituting the new values of $2B_0''$ and $w_0$ in (4) we find $\beta_0'' = 0\cdot02214$. The values of $\beta_0''$ in Table VII range between 0·0203 and 0·0217 so that equation (4) is evidently close to being fulfilled although the value of $\beta_0''$ given by it is a little too high.

In Table VIII are assembled similar data to those given in Table VII and got in a similar way for the higher final vibration levels.

In the data of Tables VII and VIII $\varepsilon$ is assumed to have the value $-\frac{1}{2}$ exactly. When this assumption is not made the corresponding constants are given in Table VI. It will be noted that the systematic variation of $\beta''$ and $2B''$ with $m$ which was observable in the $n'' = 0$ state is also present in the higher $n''$ states, so that the theoretical fit with $\varepsilon = -\frac{1}{2}$ is not perfect although it is very good. The value of $B_n''$ for different values of $n''$ is given by

$$B_n'' = 33\cdot386 - 1\cdot6497n'' + 0\cdot0212n''^2. \qquad (5)$$

Table VIII.

| $m \rightarrow$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | Mean values. ↓ |
|---|---|---|---|---|---|---|---|---|
| $F_1''(m)$ | 7·937 | 71·341 | 197·661 | 385·921 | 634·655 | 941·913 | 1305·252 | |
| $-\beta_1''$ | | 0·02113 | 0·02050 | 0·02044 | 0·01928 | | | 0·02034 |
| $2B_1''$ | 63·5107 | 63·4981 | 63·4943 | 63·4910 | 63·5350 | | | 63·5058 |
| $F_2''(m)$ | 7·540 | 67·774 | 187·774 | 366·602 | 602·855 | 894·659 | 1239·676 | |
| $-\beta_2''$ | | 0·01969 | 0·01981 | 0·01937 | 0·01919 | | | 0·01951 |
| $2B_2''$ | 60·3336 | 60·3308 | 60·3236 | 60·3281 | 60·3409 | | | 60·3314 |
| $F_3''(m)$ | 7·157 | 64·326 | 178·200 | 347·874 | 571·972 | 848·668 | | |
| $-\beta_3''$ | | 0·01922 | 0·01936 | 0·01855 | | | | 0·01904 |
| $2B_3''$ | 57·2642 | 57·2614 | 57·2537 | 57·2693 | | | | 57·2622 |
| $F_4''(m)$ | 6·780 | 60·938 | 168·798 | 329·459 | 541·561 | | | |
| $-\beta_4''$ | | 0·01848 | 0·01924 | | | | | 0·01886 |
| $2B_4''$ | 54·2502 | 54·2563 | 54·2473 | | | | | 54·2513 |

### § 4. *The Initial Rotational Levels.*

Turning to the initial levels, these are as stated already, double. The term differences for the levels from which the R′ P′ lines originate are given by

$$R'(m) - P'(m) = F'(m+1) - F'(m-1). \qquad (6)$$

These term differences have been analysed by the same methods as in dealing with the corresponding final term data. Only the results for $n' = 0$ and $n' = 2$ are given. Owing to the perturbation in the $n' = 1$ level there are not enough reliable lines for the results for this level to be certain. As in the final levels the terms are very close to the form

$$F'(m) - B'(m - \varepsilon)^2 + \beta'(m - \varepsilon)^4 \qquad (7)$$

where $\varepsilon$ is very close to $-\frac{1}{2}$. In calculating the data given in Table IX $\varepsilon$ has been assumed to be $-\frac{1}{2}$ exactly as in the similar tables for the final levels. The constants for the initial levels have very similar properties to those for the final levels. The systematic variation of $\beta'$ and $B'$ with $m$ is again quite noticeable showing that the formula does not cover the experimental data perfectly.

Table IX.

| | $F_0'(3)-F_0'(1)$ | $F_0'(4)-F_0'(2)$ | $F_0'(5)-F_0'(3)$ | $F_0'(6)-F_0'(4)$ | $F_0'(7)-F_0'(5)$ | $F_0'(8)-F_0'(6)$ | **Mean values.** |
|---|---|---|---|---|---|---|---|
| | 295·334 | 409·910 | 521·082 | 627·952 | 729·672 | 825·123 | ↓ |
| $-\beta_0'$ | 0·02118 | 0·02061 | 0·02029 | 0·01996 | 0·02001 | | 0·02041 |
| $2B_0'$ | 59·6586 | 59·6403 | 59·6329 | 59·6378 | 59·6595 | 59·6821 | 59·6519 |
| | $F_2'(3)-F_2'(1)$ | $F_2'(4)-F_2'(2)$ | $F_2'(5)-F_2'(3)$ | $F_0'(6)-F_2'(4)$ | | | |
| | 267·711 | 370·710 | 469·929 | 564·594 | | | |
| $-\beta_2'$ | 0·02432 | 0·02326 | 0·02219 | | | | 0·02326 |
| $2B_2'$ | 54·2167 | 54·1913 | 54·1914 | 54·2342 | | | 54·2084 |

It seems likely that if we put $2B_0' = 59 \cdot 65$ the last figure will not be wrong by more than 1 unit. This value compares with the following previous estimates for this quantity :—(1) 51·7 in Part V, p. 410, by the indirect method depending on the analysis of the rotation vibration cross terms. (2) 53·55 in 'Roy. Soc. Proc.,' A, vol. 114, p. 649 (1927) from the third differences of the Q lines. Both of these methods were only rough, at any rate with the data available, and the agreement is of about the kind to be expected.

Assuming the applicability of equation (7) we can now calculate the values of $F'(1)$, $F'(2)$, etc., for the upper $(P'\,R')$ levels using the mean values of $B'$ and $\beta'$. The values for the $n' = 0$ level are given in the second column of Table X. The values have been checked by recomputing the differences $F'(m+1) - F'(m-1)$ and comparing with the observed data. Except for $m = 7$ where the line may be wrong, the disagreement never exceeds 0·18 wave-number. This is greater than the observational error, but it is as good as can be expected with so simple a formula.

In the third column of Table X are given the values of $F_0'(m)$ for the upper levels from which the Q lines come. These have been got by taking the $F_0'(m)$ values in the second column and subtracting from them the values of $R'(m-1) - Q'(m-1)$, which are equal to $\underset{(P'\,R')}{F_0'(m)} - \underset{(Q)}{F_0'(m-1)}$ The differ-

Table X.

| $m$ ↓ | $F_0'(m)$. (P′, R′) | $F_0'(m)$. (Q) | $\Delta m$. | $F_0'(m)$. P′ R′ | $F_0'(m)$. Q | $\Delta m$ |
|---|---|---|---|---|---|---|
| 1 | 67·006 | 66·481 | 0·525 | 67·209 | 66·732 | 0·477 |
| 2 | 185·616 | 184·283 | 1·333 | 185·867 | 184·503 | 1·364 |
| 3 | 362·306 | 359·792 | 2·514 | 362·543 | 360·004 | 2·539 |
| 4 | 595·607 | 591·714 | 3·893 | 595·777 | 591·864 | 3·913 |
| 5 | 883·561 | 878·339 | 5·222 | 883·627 | 878·394 | 5·193 |
| 6 | 1223·715 | 1217·523 | 6·192 | 1223·654 | 1217·636 | 6·018 |
| 7 | 1613·133 | | | | | |
| 8 | 2048·387 | | | | | |

ences between the numbers in columns 2 and 3 are the doublet distances between the close pairs of upper levels shown in fig. 1. These distances are very nearly equal to ½, 1½, 2½, 3½, 4½, 5½, which are the values of $j - 1$ for the levels. In fact for the three lowest levels where the data and interpretation are most certain they only differ from $j - 1$ by amounts which might be expected from the errors and uncertainties in the calculated positions of the levels. So far as we can find from the literature* this type of doubling is usually taken to be proportional to $j \pm \varepsilon$, but this seems to be an inference from the behaviour of lines having high values of $j$, there being no reliable data for low values of $j$. For high values of $j$ the difference between $j - 1$ and $j - \frac{1}{2}$ in this separation would be indistinguishable. It seemed possible that our disagreement with this result might arise from the arbitrary assumption $\varepsilon = -\frac{1}{2}$ made in computing the data in the left-hand half of Table X. We accordingly recalculated the data, by the method already described in dealing with the final levels, without assuming $\varepsilon = -\frac{1}{2}$. This gave the values shown in columns 5, 6 and 7 of Table X. It will be seen to make very little difference to the calculated doublet distances and they agree just about as well with the values of $j - 1$.

Table XI gives the similar data for the $n' = 2$ level. As before columns 2, 3 and 4 give the values computed by assuming $\varepsilon = -\frac{1}{2}$ and columns 5, 6 and 7 corresponding values without this restriction. It will be seen that there is no great difference in the values. The chief difference between the $n' = 2$ and the $n' = 0$ levels is that in $n' = 2$ the rotational doubling is about twice as great as in $n' = 0$. The separations $\Delta_m$ are still proportional to 1 : 3 : 5 : 7 : 9 ; so that for these 3P states at any rate the rotational doubling is proportional to the $j - 1$ values.

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* *E.g.*, Mulliken, 'Phys. Rev.,' vol. 28, p. 485 (1926).

Table XI.

| $m$ ↓ | $F_2'(m)$. (P′ R′) | $F_2'(m)$. (Q) | $\Delta m$. | $F_2'(m)$. (P′ R′) | $F_2'(m)$. (Q) | $\Delta m$. |
|---|---|---|---|---|---|---|
| 1 | 60·866 | 59·872 | 0·994 | 61·253 | 60·333 | 0·920 |
| 2 | 168·492 | 165·883 | 2·609 | 168·953 | 166·290 | 2·663 |
| 3 | 328·536 | 323·800 | 4·736 | 328·964 | 324·201 | 4·763 |
| 4 | 539·322 | 532·446 | 6·876 | 539·664 | 532·798 | 6·866 |
| 5 | 798·618 | 790·061 | 8·557 | 798·894 | 790·395 | 8·499 |
| 6 | 1103·631 |  |  | 1103·956 |  |  |

Owing to the perturbation in the 1′ level it is not possible to supply similar detailed information but it is possible to say something about it. Of the lines which come from this vibration level the Q lines and the lines R′ (0), R′ (1), R′ (2), P′ (2), P′ (3), P′ (4) are certain. The only combination of these which gives an upper term properly is R′ (2) − P′ (2) = F (3) − F (1). If we compare this with the value of the same rotational term for the three other upper vibrational levels we have :—for $n' = 0$, 295·334 ; for $n' = 1$, 272·160 ; for $n' = 2$, 267·705 ; and for $n' = 3$, 254·390. The successive differences of these numbers are 23·174, 4·455 and 13·315. Thus this term difference for the $n' = 1$ level is irregular being about 8 wave-numbers lower than the value which would fit in regularly with the others. Another way in which this level is abnormal is brought out if we consider the relation between the P′ R′ and the Q levels.

Table XIa.

| $m$ → | 1. | 2. | 3. | 4. | 5. | $n'$ ↓ |
|---|---|---|---|---|---|---|
| R′ ($m$) − Q ($m$) .................... | 119·12 | 178·05 | 235·76 | 291·73 | 345·30 | 0′ |
| Q ($m$ + 1) − P′ ($m$ + 1) .... | 117·31 | 174·15 | 229·32 | 282·65 |  |  |
| R ($m$)′ − Q ($m$) .................... | 110·15 | 160·06 |  |  |  | 1′ |
| Q ($m$ + 1) − P′ ($m$ + 1) .... | 112·09 | 168·19 | 226·58 |  |  |  |
| R′ ($m$) − Q ($m$) .................... | 108·63 | 162·67 | 215·46 | 266·13 | 313·71 | 2′ |
| Q ($m$ + 1) − P′ ($m$ + 1) .... | 105·06 | 155·26 | 203·86 | 250·85 |  |  |
| R′ ($m$) − Q ($m$) .................... | 104·76 | 155·97 | 206·68 | 256·76 |  | 3′ |
| Q ($m$ + 1) − P′ ($m$ + 1) .... | 98·42 | 145·14 | 191·01 |  |  |  |

The values of R′ $(m)$ — Q $(m)$ and Q $(m+1)$ — P′ $(m+1)$ are set out, from each of the four upper levels 0, 1, 2, 3 in Table XIA. The difference between R′ $(m)$ — Q $(m)$ and Q $(m+1)$ — P′ $(m+1)$ is the quantum defect caused by the doubling and crossing over of the upper levels. It will be observed that for $n' = 0$, 2 and 3, R′ $(m)$ — Q $(m)$ is always > Q $(m+1)$ — P $(m+1)$, but in the perturbed 1′ level it is less. In fact in the $n' = 1$ vibration level the Q levels for a given $j$ are not below the P′ R′ level for the same $j$ as shown in fig. 1 but they lie above them. We shall see in a moment that exactly the same thing is true of the upper levels of the $H_\beta$ bands which also are weak.

The only term values for the $n' = 3$ level are R′ (2) — P′ (2) = 254·390 and R′ (3) — P′ (3) = 351·785. These give $B_3 = 25{\cdot}628$ and $\beta_3 = -0{\cdot}0259$.

### § 5. *The Upper Levels of the* $H_\beta$ *Bands.*

The data are too fragmentary to do much with except in the case of the $n' = 0$ vibration state. The observed data for this state are

F′ (3) — F′ (1) = 289·39, F′ (4) — F′ (2) = 401·12, R′ (1) — Q (1) = 116·15, R′ (2) — Q (2) = 172·48, R′ (3) — Q (3) = 226·48, Q (2) — P′ (2) = 116·91, Q (3) — P′ (3) = 174·64 and Q (4) — P′ (4) = 231·60.

The R′, Q differences are less than the Q, P′ differences ; it is the other way about in the $H_\alpha$ bands, except when $n' = 1$. If we make the calculations assuming $F'(m) = B_0'(m - \varepsilon)^2 + \beta_0'(m - \varepsilon)^4$ and assume $\varepsilon = -\frac{1}{2}$ exactly we have $-\beta_0 = 0{\cdot}0240$. This gives two values of $2B_0'$, viz., 58·574 and 58·575, mean 58·5745. Using these we calculate column 2 of Table XII.

Table XII.

| $m$ ↓ | $F_0'(m)$ (P′ R′). | $F_0'(m)$ (Q) | $-\Delta(m)$. |
|---|---|---|---|
| 1 | 65·774 | 65·96 | 0·19 |
| 2 | 182·108 | 182·685 | 0·58 |
| 3 | 355·167 | 356·750 | 1·58 |
| 4 | 583·226 | 586·77 | 3·54 |

The values of $-\Delta m$ would agree better with $-\frac{1}{2}$, $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$ or 0, 1, 2, 3, than with $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, $3\frac{1}{2}$ as the highest value should have the largest error. Unfortunately there are not enough data to determine the value of $\varepsilon$ independently and as this level has some of the properties of the perturbed $n' = 1$ level of the $\alpha$ bands there may be some inherent irregularity in it which would nullify any general conclusions about the values of $\Delta m$ which might be drawn from it.

## § 6. *The* 2S — 3S *Bands.*

There is a system of bands in the red and infra-red which have the same final states as the $H_{\alpha, \beta, \gamma, \text{etc.}}$, bands. The lines with the final and initial vibration and rotational term differences are given in Table XIII and XIV. The final term differences are the same as those of the $\alpha$, $\beta$, $\gamma$ bands so that the final state is the one we have denoted by $2\,{}^3S$. The initial states, however, are different from any hitherto encountered. The bands are characterised by the presence of P and R branches of about equal intensity and by the absence of Q branches. The line P (1) (see the diagram on the right-hand side of fig. 1) is present; so that there is a lower level in the upper state than the lowest level in the $m$P states of the $\alpha$, $\beta$, $\gamma$ bands. The upper levels of these bands are therefore $m$S levels (they are all single) and from the value of $\nu_0$ for the bands it is almost certain that $m = 3$. We shall therefore refer to them provisionally as $3\,{}^3S$ levels.

As the final level has already been analysed we are now only interested in the initial level. The rotational terms of this level appear to be represented by $F(m) = B(m - \varepsilon)^2 + \beta(m - \varepsilon)^4$ with $\varepsilon = -\frac{1}{2}$ to the accuracy of the observational data. The values got in this assumption are shown in Table XV.

Table XIII.—

New Bands ($^3$S → $^3$S, Q Branch absent,

| *m* | 0, 0 | | 0, 1 | | | | |
|---|---|---|---|---|---|---|---|
| 0 | †15642·48 (1) | 2524·28 | 13118·2 (1) | | | | |
| 1 | *15669·39 (4) | 2521·09 | 13148·3 (4) | | | | |
| 2 | 15076·02 (1) | 2514·52 | 13161·5 (0*a*) | | | | |
| 3 | †15662·53 (2) | 2504·83 | 13157·7 (1) | | | | |
| 4 | 15629·10 (00) | | | | | | |
| *m* | 1, 0 | | 1, 1 | | 1, 2 | | |
| 0 | | | 14904·35 (1) | 2388·25 | 12516·1 (00) | | |
| 1 | 17449·52 (1) | 2521·03 | 14928·49 (3) | 2385·09 | 12543·4 (2*b*) | | |
| 2 | | | 14932·73 (1) | 2378·73 | 12554·0 (0*b*) | | |
| 3 | | | †14917·11 (1*a*) | 2369·41 | 12547·7 (1*a*) | | |
| 4 | | $_7a_7$ Q1 = | 14885·15 (1*a*) | | 12527·9 (00) | | |
| *m* | | | | | 2, 2 | | 2, 3 |
| 0 | | | | | 14157·9 (1) | 2255·9 | 11902·0 (00) |
| 1 | | | | | 14181·3 (3) | 2253·1 | 11928·2 (2) |
| 2 | | | | | 14188·5 (1) | 2246·8 | 11941·7 (00*c*) |
| 3 | | | | | | | |

R Branches.

and no missing line except the null point).

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| m | 1′–0′ | | |
|---|---|---|---|
| 0 | 1786·15 | | |
| | | 5·96 | |
| 1 | 1780·19 | | 3·00 |
| | | 8·96 | |
| 2 | 1771·23 | | 2·86 |
| | | 11·82 | |
| 3 | 1759·41 | | |

| 2′–1′ | |
|---|---|
| 1641·8 | |
| | 3·9 |
| 1637·9 | |
| | 3·4 |
| 1634.5 | |

| m | 0, 1 | | |
|---|---|---|---|
| 1 | 13118·2 | | |
| | | 30·1 | |
| 2 | 13148·3 | | 16·9 |
| | | 13·2 | |
| 3 | 13161·5 | | 17·0 |
| | | –3·8 | |
| 4 | 13157·7 | | |

| 1, 2 | | |
|---|---|---|
| 12516·1 | | |
| | 27·3 | |
| 12543·4 | | 16·7 |
| | 10·6 | |
| 12554·0 | | 16·9 |
| | –6·3 | |
| 12547·7 | | |

| 0, 0 | | |
|---|---|---|
| 15642·48 | | |
| | 26·91 | |
| 15669·39 | | 20·28 |
| | 6·63 | |
| 15676·02 | | 20·12 |
| | –13·49 | |
| 15662·53 | | 19·94 |
| | –33·43 | |
| 15629·10 | | |

| 1, 1 | | |
|---|---|---|
| 14904·35 | | |
| | 24·14 | |
| 14928·49 | | 19·90 |
| | 4·24 | |
| 14932·73 | | 19·86 |
| | –15·62 | |
| 14917·11 | | |

Final Term Differences.

| | 0″ | 1″ | 2″ | 3″ |
|---|---|---|---|---|
| R (0) – P (2) = | 199·42 | 189·71 | 180·2 | 171·2 |
| " (1) – " (3) = | 330·78 | 314·52 | 298·85 | 283·6 |
| (2) – (4) = | 459·40 | 436·89 | 415·1 | 393·8 |
| (3) – (5) = | 584·62 | 555·86 | 528·0 | |

Initial Term Differences.

Not Mean.

| | 0′ | | | |
|---|---|---|---|---|
| R (1) – P (1) | 140·47 | | | |
| | | 92·49 | | |
| | 232·96 | | 1·53 | |
| | | 90·96 | | 0·87 |
| | 323·92 | | 2·40 | |
| | | 88·56 | | |
| | 412·48 | | | |

| 1′ | | |
|---|---|---|
| 131·48 | | |
| | 86·61 | |
| 218·09 | | 1·56 |
| | 85·05 | |
| 303·14 | | |

| 2′ | |
|---|---|
| 125·2 | |
| | 85·6 |
| 210·8 | |

## Table XIV.—

New System ($^3S \rightarrow {}^3S$ Q Branch absent,

| *m* | 0, 0 | | 0, 1 | | | | |
|---|---|---|---|---|---|---|---|
| 1 | 15528·92 (3) | 2521·02 | 13007·9 (2) | | | | |
| 2 | 15443·06 (2) | 2514·56 | 12928·5 (2) | | | | |
| 3 | *15338·61 (3) | 2504·81 | 12833·8 (4) | | | | |
| 4 | 15216·62 (0*a*) | 2492·02 | 12724·6 (1) | | | | |
| 5 | 15077·91 (0) | 2476·01 | 12601·9 (2*a*) | | | | |
| *m* | 1, 0 | | 1, 1 | | 1, 2 | | |
| 1 | 17318·03 (0) | 2521·02 | 14797·01 (3) | 2385·11 | 12411·9 (2) | | |
| 2 | 17229·24 (0) | 2514·60 | 14714·64 (3) | 2378·74 | 12335·9 (1) | | |
| 3 | 17118·79 (1) | 2504·82 | 14613·97 (3) | 2369·37 | 12244·6 (3) | | |
| 4 | | | 14495·86 (2) | 2356·96 | 12138·9 (1) | | |
| 5 | | | 14361·19 (1) | 2341·49 | 12019·7 (1) | | |
| *m* | 2, 0 | | 2, 1 | | 2, 2 | | 2, 3 |
| 1 | | | | | 14056·1 (1) | 2253·0 | 11803·1 (0) |
| 2 | 18870·92 (0) | 2514·48 | 16356·44 (0*h*) | 2378·74 | 13977·7 (0*a*) | 2246·9 | 11730·8 (1*c*) |
| 3 | 18756·76 (0) | 2504·97 | 16251·79 (4) | 2369·39 | 13882·4 (1) | 2237·8 | 11644·6 (00*a*) |
| 4 | 18622·51 (1) | 2492·04 | ${}_0a_0P6$<br>16130·47 (2) | | | | 11547·9 (1) |

## Table XV.

| $m \rightarrow$ | 0. | 1. | 2. | 3. | 4. | 5. | Mean values ↓ |
|---|---|---|---|---|---|---|---|
| $F_0'(m+2) - F_0'(m)$ (obs.) .... | 140·46 | 232·98 | 323·91 | 412·48 | | | |
| $-\beta_0'$ .................................... | 0·01525 | 0·01263 | 0·01381 | | | | 0·0139 |
| $2B_0'$ .................................... | 47·001 | 46·979 | 47·010 | 47·013 | | | 47·001 |
| $F_0'(m)$ .................................... | 5·88 | 52·80 | 146·33 | 285·79 | 479·18 | 698·16 | |
| $F_0'(m+2) - F_0(m)$ (calc.) .... | 140·45 | 232·99 | 323·85 | 412·37 | | | |
| $F_1'(m+2) - F_1(m)$ (obs.) .... | 131·47 | 218·12 | 303·15 | | | | |
| $-\beta_1'$ .................................... | 0·0124 | 0·0132 | | | | | 0·0128 |
| $2B_1'$ .................................... | 43·989 | 43·995 | 43·985 | | | | 43·990 |
| $F_1'(m)$ .................................... | 5·50 | 49·43 | 136·97 | 267·52 | 440·15 | | |
| $F_1'(m+2) - F_1'(m)$ (calc.) .... | 131·47 | 218·09 | 303·18 | | | | |

P Branches.

and no missing line except the null point).

| m | Mean 1′−0′ | | | Mean 2′−1′ | | |
|---|---|---|---|---|---|---|
| 1 | 1789·11 | | | 1644·20 | | |
| | | 2·93 | | | 2·40 | |
| 2 | 1786·16 | | 3·03 | 1641·80 | | 1·59 |
| | | 5·98 | | | 3·99 | |
| 3 | 1780·18 | | 2·94 | 1637·81 | | |
| | | 8·92 | | | | |
| 4 | 1771·26 | | 3·05 | | | |
| | | 11·97 | | | | |
| 5 | 1759·29 | | | | | |

| 0, 0 | | | 1, 1 | | | 2, 2 | | |
|---|---|---|---|---|---|---|---|---|
| 15528·92 | | | 14797·01 | | | 14056·1 | | |
| | 85·86 | | | 82·37 | | | 78·4 | |
| 15443·06 | | 18·59 | 14714·64 | | 18·30 | 13977·7 | | 16·9 |
| | 104·45 | | | 100·67 | | | 95·3 | |
| 15338·61 | | 17·54 | 14613·97 | | 17·44 | 13882·4 | | |
| | 121·99 | | | 118·11 | | | | |
| 15216·62 | | 16·72 | 14495·86 | | 16·56 | | | |
| | 138·71 | | | 134·67 | | | | |
| 15077·91 | | | 14361·19 | | | | | |

| 0, 1 | | | 1, 2 | | | 2, 3 | | |
|---|---|---|---|---|---|---|---|---|
| 13007·9 | | | 12411·9 | | | 11803·1 | | |
| | 79·4 | | | 76·0 | | | 72·3 | |
| 12928·5 | | 15·3 | 12335·9 | | 15·3 | 11730·8 | | 13·9 |
| | 94·7 | | | 91·3 | | | 86·2 | |
| 12833·8 | | 14·5 | 12244·6 | | 14·4 | 11644·6 | | 10·5 |
| | 109·2 | | | 105·7 | | | 96·7 | |
| 12724·6 | | 13·5 | 12138·9 | | 13·5 | 11547·9 | | |
| | 122·7 | | | 119·2 | | | | |
| 12601·9 | | | 12019·7 | | | | | |

This band system shows an alternation in intensity of the successive lines like that found in the α, β, γ systems. This is quite clear from Gale, Monk and Lee's intensity estimates. Owing to so much of the system being in the infra-red only a few of the stronger lines have been measured by Kapuscinski and Eymers. As in the α bands the strong lines are those with odd suffixes P (1), P (3), . . ., R (1), R (3), . . ., etc, P (2), P (4), . . ., R (0), R (2), . . ., etc., being weak and the weight ratio is evidently roughly 3 to 1. All the lines which occur are precisely accounted for by the scheme on the right of fig. 1, using the restrictions $\Delta j = 0$ or $\pm 1$ and $s \not\rightleftarrows a$. The absence of Q branches is accounted for by the fact that $\Delta j = 0$ is not allowed to operate as it would conflict with $s \not\rightleftarrows a$.

We shall now calculate the value of $\nu_0$, the frequency of the null line, *i.e.*, the frequency which corresponds to the purely electronic transitions in the band. In the $0 \rightarrow 0$ band the frequency of the R (0) line will be given by

$\nu = \nu_0 + F'(1) - F''(0)$, R (1) by $\nu = \nu_0 + F'(2) - F''(1)$, and so on. Using the $F''$ data in Table VII and the $F'$ data in Table XV we obtain from R (1), R (2) and R (3) the respective values 15598·02, 15598·07, 15598·07 mean 15598·05. By the same method from P (1), P (2) and P (3) we get $\nu_0 = 15598{\cdot}05$, 8·10 and 8·10 mean 15598·08. The value for the $2^3S - 3^3P$ system calculated in Part V was 16619·44. We can recalculate this, using the more accurate term data of the present paper. For this system using R′ (0), R′ (1), R′ (2) we get $\nu_0 = 16619{\cdot}96$, 9·93, 9·97 mean 16619·95, using P′ (2), P′ (3) 16619·89, 9·99 mean 16619·94, and using Q (1), Q (2) Q 16619·96, 9·93, 9·97 mean 16619·95. Thus the value of $\nu_0$ for this system is the same both for the Q and the P′ and R′ branches to the accuracy of the observational data. If we make similar calculations for the $2^3S - 4^3P\,(H_\beta)$ system we have from R (0), R (1), R (2) $\nu_0 = 22272{\cdot}37$, 2·30, 2·36 mean 22272·34, from P (2), P (3) 22272·37, 2·37 mean 22272·37, and from Q (1), Q (2), Q (3) 22272·25, 2·36, 2·38 mean 22272·30. Here again there is no sure difference in the $\nu_0$'s as determined by the different branches.

We can now give approximately the value of the $3\,^3S$ term. In Part V it was shown that the Q (1) lines of $2\,^3S - m\,^3P$ were closely represented by $2\,^3S = 29340{\cdot}3$, $3\,^3P = 12718{\cdot}87$, $4\,^3P = 7067{\cdot}07$, etc., and as the null lines are in all cases $9 \pm 1$ wave-numbers higher than the corresponding $0 \rightarrow 0$ Q (1) lines in these systems we take the $2\,^3S$ term to be 29340. This gives approximately the same values for the null lines of $2\,^3S - m\,^3P$ as in Part V and also it gives $3\,^3S = 13742$. This is about 1000 more than the corresponding $2\,^3P$ term, the difference being less than in the orthohelium spectrum but in the same direction. If we divide these into the Rydberg constant we get for the denominator of $2\,^3S$ 1·933 and of $3\,^3S$ 2·822. The corresponding terms measured from the lowest $H_2$ $1\,^1S$ term, as by Birge,[*] would be $2\,^3S = 94897$ and $3\,^3S = 110495$.

## § 7. *The Vibrational Terms.*

For the α system the vibrational terms are given more accurately than the values already used by the formulæ

$$w_n'' = 2594{\cdot}03\,n - 70{\cdot}554\,n^2 + 0{\cdot}9723n^3 - 0{\cdot}04958\,n^4$$

and

$$w_n' = 2307{\cdot}52\,n - 65{\cdot}013\,n^2 + 0{\cdot}845\,n^3 - 0{\cdot}029\,n^4.$$

In the case of the initial terms the formula represents the data to the accuracy of the observations. The comparison is shown in the following table, in which the observed values have been obtained by adding $\frac{9}{8}$ of the second differences 3·24, etc., to the vibration differences for $m = 1$ lines, and so obtaining a longer series of differences than if R (0) lines were used. The second differences 3·24, etc., are represented by the formula :—*n*th second difference $= 3{\cdot}24 - 0{\cdot}07\,n$.

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[*] 'Proc. Nat. Acad. Sci.,' vol. 14, p. 12 (1928).

| Term ........ | 1″ – 0″ | 2″ – 1″ | 3″ – 2″ | 4″ – 3″ | 5″ – 4″ | 6″ – 5″ | 7″ – 6″ |
|---|---|---|---|---|---|---|---|
| Calculated | 2524·40 | 2388·43 | 2256·50 | 2127·47 | 2000·05 | 1873·15 | 1745·52 |
| Observed .... | 2524·72 | 2388·69 | 2256·54 | 2127·26 | 1999·90 | 1873·05 | 1745·36 |
| Term ........ | 1′ – 0′ | 2′ – 1′ | 3′ – 2′ | 4′ – 3′ | 5′ – 4′ | 6′ – 5′ | 7′ – 6′ |
| Calculated | 2243·43 | 2117·86 | 1996·62 | 1878·62 | 1763·24 | 1649·82 | 1537·62 |
| Observed .... | 2243·51 | 2118·01 | 1993·65 | 1878·56 | 1762·96 | 1649·92 | 1537·62 |

We have already investigated the validity of the equation $\beta_0 = B_0\,(2B_0c/w_0)^2$ for the 2 $^3$S level. For the 3 $^3$P level from which the R′ and P′ lines spring we find $w_0x = 61{\cdot}68_5$ compared with 62·94 got for the Q levels in Part V and for $w_0$ 2307·63 compared with 2306·94 for the Q levels in Part V. Putting this and $2B = 59{\cdot}65$ in $\beta = B_0(2B_0c/w_0)^2$ gives $\beta_0 = 0{\cdot}0199$. This compares with the more directly determined value already found of $0{\cdot}0204_1$ which was the mean of 0·02118, 0·02061, 0·02029, 0·01996 and 0·02001.

For 4 $^3$P there are not enough data to determine $w_0$ directly so we take the value 2276·45 for the Q levels in Part V as accurate enough. This is seen to be legitimate because the vibrational difference 1, 1 R′ (1) – 0, 1 R′ (1) = 2204·68 is practically the same as that of 1, 1 Q′ (1) – 0, 1 Q (1) = 2203·07 in Part V. Putting this and $2B_0 = 58{\cdot}574_5$ in the preceding formula gives $\beta_0 = 0{\cdot}01945$. This compares with the value already deduced, from very meagre data and assuming $\varepsilon = -\frac{1}{2}$, of $\beta = 0{\cdot}0240$.

In the case of 3 $^3$S we have not yet determined $w_0$. Using the P (1) lines we have the formula

$$\mathrm{P}\,(1)\,n_1'\,n'' - \mathrm{P}\,(1)\,n_2'\,n'' = \tfrac{1}{4}\,\alpha'\,(n_2' - n_1') + w_0'\,[n_1'\,(1 - x'n_1' + \ldots) \\ - n_2'\,(1 - x'n_2'\,\ldots)].$$

The first two differences 1789·11 and 1644·20 give, taking $\alpha' = 1{\cdot}6$, $w_0'x' = 72{\cdot}45_5$, $w_0 = 1861{\cdot}96$. On substituting this and $2B_0 = 47{\cdot}001$ in the formula we find $\beta_0 = 0{\cdot}01497$. This compares with the value already deduced of 0·0140 which was the mean of 0·01525, 0·01263 and 0·01381.

### § 8. *Various Constants.*

Using $h = 6 \cdot 55 \times 10^{-27}$, $c = 3 \cdot 000 \times 10^{-10}$ and the mass of the hydrogen atom $= 1 \cdot 662 \times 10^{-24}$ we have the values of the band constants $2B_0$ and $\beta_0$ (assuming $\varepsilon = -\frac{1}{2}$ exactly), of the moment of inertia $I_0$ and of the nuclear distance $r_0$ for the various excited hydrogen molecules designated by $2\,^3S$, $3\,^3S$, $3\,^3P$ (Q states), $3\,^3P$ (R′ states), $4\,^3P$ (Q states), and $4\,^3P$ (R′ states), which are shown in the following table :—

| State.<br>↓ | $2B_0$. | $-\beta_0$. | $I_0$. | $r_0$. |
|---|---|---|---|---|
| $2\,^3S$ ........................ | 66·773 | 0·02100 | $8 \cdot 277 \times 10^{-41}$ | $0 \cdot 9980 \times 10^{-8}$ |
| $3\,^3S$ ........................ | 47·001 | 0·0140 | 11·176 | 1·190 |
| $3\,^3P$ (Q) .................. | 59·09 | 0·0179 | 9·354 | 1·061 |
| $3\,^3P$ (R′) ............... | 59·65 | 0·0204 | 9·266 | 1·056 |
| $4\,^3P$ (Q) .................. | 58·80 | 0·0190 | 9·401 | 1·064 |
| $4\,^3P$ (R′) ............... | $58 \cdot 574_5$ | 0·02 | 9·436 | 1·066 |

# OBITUARY NOTICES.

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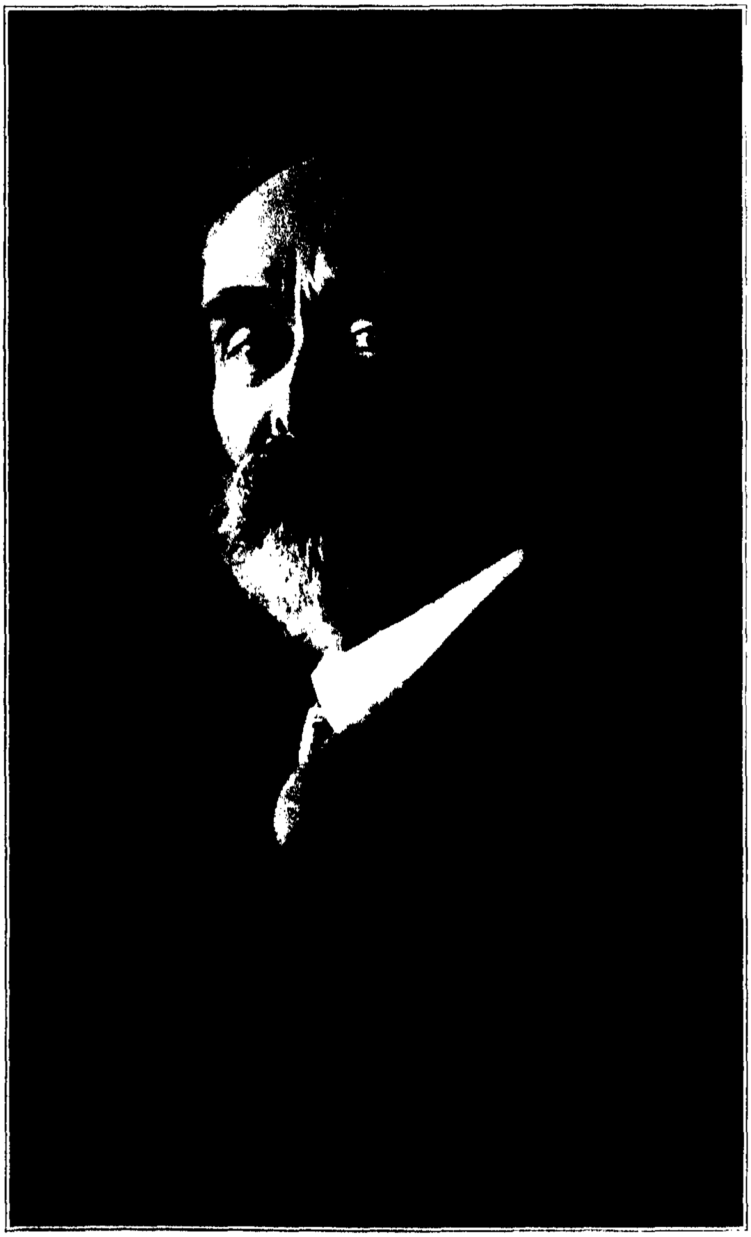

H. R. PROCTER.

*(By permission, from the Journal of the Chemical Society.)*

# HENRY RICHARDSON PROCTER, 1848-1927.

Among the men of science who have devoted themselves to the improvement of our manufacturing arts, the subject of this notice, Henry Richardson Procter, acclaimed on every side as the pioneer of a scientific leather industry, occupies a conspicuous place of honour. His death has evoked tributes from all parts of the world acknowledging his services to the industry and celebrating his qualities as a scientific investigator, a teacher, and a man rich in qualities of mind and heart.

Henry Richardson Procter was born on May 6, 1848, at Lowlights, North Shields, his parents both being descendants of the Quaker and tanning family of Richardson. His father maintained the old tannery and designed that Henry, his elder son, should succeed him. At the age of 14 Procter went to Bootham School, York, where, according to an autobiographical note, he had more training in science, for which he already showed an aptitude, than was common in schools of that day. After leaving school he was apprenticed to his father's business and made some efforts to apply his chemical knowledge to tanning, carrying on his scientific studies in an attic laboratory. Having passed the Government " South Kensington " Chemistry Examination, and so become a qualified teacher, he taught a small chemistry class in the town and in connexion therewith was invited to a week's summer course at the Royal College of Chemistry in Oxford Street, London. There his talents so impressed the authorities that they persuaded him to return to London at Christmas for the rest of the term. At the end of the course he was head of the lists and obtained the full certificate. During part of this time he acted as volunteer assistant to Edward Frankland and Norman Lockyer and so became interested in astronomy. He also published, in conjunction with his relative, T. H. Waller, a translation of Kohlrausch's " An Introduction to Physical Measurements," one of the earliest laboratory books of practical physics to be generally used in this country.

Reluctantly refusing Lockyer's invitation to join the Eclipse expedition, then proceeding to India, Procter returned to his father's tannery and set to work with success in improving and expanding the manufacture. He had little taste for the business side of the industry and as competition within it had become very acute by the time his father died in 1888, he abandoned the paternal tannery and took up the post of chemist to the tanning firm of his relatives, Messrs. S. and J. Richardson, of Elswick, Newcastle-on-Tyne. Here he remained until, in 1890, he was invited by the Yorkshire College, Leeds, to take direction of a new department of applied chemistry which it had been decided to establish for the benefit of the leather industries. The offer, from a worldly point of view, was meagre, but happily the possession of some private means enabled Procter to seize what was to him a tempting opportunity of living in the scientific world and of devoting himself unrestrictedly to scientific work. He took up his post at Leeds early in 1891 and began with very simple accommodation and appliances to devise a course of instruction in the applied science of leather manufacture. In 1898 his department was transferred to a new building provided by the generosity of the Worshipful Company of Skinners of London. These excellent premises were laid out after Procter's design for teaching and research, and they included manufacturing plant on a scale sufficient to afford demonstrations and trials on a valid working scale.

In setting up this new department of applied science, Procter was confronted with the usual difficulty of securing students of adequate preliminary education and intellectual quality. He would have been glad indeed if he could have insisted that students coming to him had previously been equipped fully in fundamental sciences. His own educational and scientific standards were very high, but he was no pedant; he had sympathy with people whose outlook was strongly practical, and his teaching afforded a striking example of the way in which an interest and schooling in scientific theory and scientific method can be inculcated by an approach from the side of practical problems. It could often be seen how under his guidance and the stimulus of a visible practical end, students previously reluctant would awaken to a perception of the value of chemical theory and apply themselves with zeal to serious scientific study. He produced by his three years' course a type of student well trained to address himself to the scientific control and development of the processes of leather manufacture. Students soon came to Procter from all parts of the world and returned to put to effective use the training which they had received.

Before taking up work at Leeds, Procter had gone far towards bringing science to play its due part in the leather industry. His 'Text-Book of Tanning,' published in 1885, was the first serious effort in the application of science in tannery practice, and is recognized as having inaugurated a scientific era in the industry. It embodies a great deal of original work which he had done since the first publication, in his twenties, of papers on tannin analysis. The difficulty of applying scientific methods to the leather industry came at the outset in the basic substance of the old tannery process—What is tannin and how is the tanning value of a substance to be estimated for the purpose of both manufacture and commerce? The first question can only be answered in the vaguest way. There are many tannins, but they present great chemical variety and not much is known about their constitution. They are all derivatives of the aromatic series of carbon compounds, and, so far as is known, all contain either pyrocatechol or pyrogallol, and sometimes phloro-glucinol.

The pyrogallol tannins yield gallic acid as a decomposition product and many of them glucose. The pyrocatechol tannins contain protocatechuic acid and seem to yield no glucose. The tannins have the one common property of converting skins into leather, and for any scientific control of leather manufacture a standard method of estimating the tanning efficacy, one which will give reproducible results in different hands, is indispensable.

It was to this end that Procter's first efforts were directed, and he devoted great labour to developing the method based on the use of hide powder. During fifty years he returned continually to the subject, and he took the principal part as Chairman of the International Commission in drawing up the official method of tannin analysis, published by the International Association of Leather Trades Chemists in 1907. In the new international method adopted last year the essential principles of the earlier one are retained.

Apart from his work on tannin analysis, Procter concerned himself with devising simple methods of chemical control for the various operations of the tan-yard, and in his laboratory the biological as well as the chemical aspect of tanning problems was always the subject of study. He took a very active part in the establishment of chrome tanning. He gave to the trade his well-known formula for the making of single-bath chrome liquors, and his teaching of the scientific principles of the new methods contributed in a very important way to their adoption and success.

Behind all Procter's active work of the kind just described was the constant occupation of his mind with the fundamental science of colloids. He showed in relation to the newer physical chemistry his remarkable power of bringing himself fully abreast of the times in any special part of theoretical science that he wanted to use, and so equipped he entered upon his *magnum opus*. This was a very complete investigation of the conditions determining the state of equilibrium which is established when gelatin jellies are brought into contact with solutions of acids.* The attainment of equilibrium in such systems is usually associated with swelling or contraction effects which depend on the nature and concentration of the acid solution and are also affected by the presence of neutral salts.

Procter recognised clearly that such a system is one to which the Donnan theory of membrane equilibria can be applied. In virtue of its basic properties, gelatin combines with acids to form gelatin salts ; on ionisation these yield a gelatin kation which is of relatively very large dimensions and consequently unable to pass through membranes which are readily permeable to ionic or molecular entities of smaller size. The interface between a gelatin jelly and its aqueous environment may be regarded as the equivalent of an actual membrane for the gelatin ions are necessarily confined to the jelly side of the interface, whereas the anions associated with the gelatin kations may pass freely from one side to the other under the influence of osmotic forces, subject, of course, to such restrictions as are attributable to the intervention of electrical forces between the charged ions.

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* The writer has to thank Prof. H. M. Dawson for summarising this work. He is also indebted to Mr. W. R. Atkin and Mr. F. C. Thompson of the Leather Industries Department of Leeds University for valuable assistance.

When a gelatin jelly is immersed, for instance, in a solution of hydrochloric acid, the latter passes through the interface, forming the salt gelatin hydrochloride, and ultimately a state of equilibrium is established in which we have gelatin ions, hydrogen ions, and chlorine ions on the jelly side of the interface, whilst hydrogen ions and chlorine ions are in the outer solution. In accordance with Donnan's theory, it follows that the osmotic pressure within the jelly must be greater than that of the outer solution, and Procter recognized in this inequality the cause of the swelling which, according to his views, proceeds until the difference in the osmotic pressures is counterbalanced by the forces of cohesion in the gel.

This theory, elaborated subsequently in conjunction with J. A. Wilson, has been found to give a satisfactory account of the phenomena associated with the swelling of gelatin, and affords a very notable example of the successful application of the theory of membrane equilibria. The significance of his work from a purely scientific point of view is to be found in the highly satisfactory issue of this attempt to deal with a problem which, even in its essential outlines, had previously been quite obscure. As a result of his investigations, this type of problem was brought within the range of application of modern physico-chemical principles, and in this way he provided a rational basis for the further investigation of colloid systems which is recognised to be of the greatest importance from the purely scientific as well as from the technical point of view. The late Jacques Loeb wrote of Procter's theory of protein swelling as " one of the most ingenious and original contributions to modern science."

Of Procter's contributions to the literature of his subject the 'Text-Book of Tanning' has already been mentioned. This was followed in 1898 by the publication of the 'Leather Industries Laboratory Book' and in 1903 by the 'Principles of Leather Manufacture.' The 'Principles' at once took the position which it has retained, that of a standard masterpiece of applied science literature. It has been translated into many languages, including Japanese.

For a full account of Procter's work and the testimony of those who profited from it, the reader is referred to the " Procter Memorial Issue " of the 'Journal of the International Society of Leather Trades' Chemists.' Typical of this testimony may be quoted the words of Professor V. Kubelka of Brünn, who, after expressing his own indebtedness, says : " Je suis certain qu'il y a dans tous les pays du monde des centaines de chemistes de cuir qui se rappelleront avec reconnaissance que pour eux aussi les libres de H. Procter étaient les premiers phares qui les ont conduit dans l'étude de la chimie de cuir." A list of 121 publications gives some idea of the variety of Procter's scientific work and the range of his technical services. Among these services was the foundation in 1897 of the Society just mentioned, which from small beginnings grew to include all the leather chemists of Europe and in other and more remote countries. Procter was its first President and always its central influence.

Procter held his professorship at Leeds until, in 1913, he reached the age of retirement. In anticipation of this event steps had been taken by the leather industry to mark the event by some suitable memorial of the man and his services. The story may perhaps be best expressed in Procter's words: "On my retirement in 1913 a considerable sum, over £1,800, was subscribed by my friends as an acknowledgment of what I had done for the chemistry of the trade, and as I have fortunately a modest independent income, I thought that this (the fund) could be most usefully devoted to the establishment of a special laboratory to investigate the underlying scientific problems, which though not likely to be of immediate commercial value, are yet the materials on which sound advance can be based. The money sufficed to erect the laboratory, but unfortunately not to endow it, but it is now open to qualified students of all nations at fees calculated merely to cover their actual cost, and the University, which acts as a Trustee under a Deed-poll, has so far generously borne a good part of the actual working expenses. With more money and more research students, its usefulness might be greatly increased."

Procter's successor, in the person of Dr. E. Stiasny, had already been chosen and had been acting for some time with great success as assistant professor. He now took the vacant Chair and Procter passed into the new Research Laboratory, where with J. A. Wilson he completed his work on gelatin. The formal opening of the Laboratory by Sir William Ramsay and the attendance of representatives of the industry from all parts of the world was to have taken place in October, 1914. To this plan the outbreak of war put an end. Not only so, but in August Prof. Stiasny was in Austria, his native country. In this emergency, Prof. Procter resumed his old position and busied himself with important work for the War Office, remaining in office till 1918. He was then succeeded by his old pupil, Prof. McCandlish, but he continued to work a good deal in his laboratory. In 1923 he sold his house at Ilkley and retired to Newlyn, Cornwall, where, in proximity to his artist son, Ernest, he spent the evening of his life in comfort and content, pursuing old hobbies of handicraft and art and enjoying the society of friends. Towards the end of 1926 he was compelled to take to his bed, and he died on August 17, 1927. He was buried at St. Hilary, some miles from Penzance.

Procter had married in 1874 Emma Watson of Newcastle, who died in 1901. He has left a daughter and two sons, the elder, Mr. J. W. Procter, a distinguished architect, the younger the well-known artist, Mr. Ernest Procter.

Procter's success and the sway which he acquired were largely bound up with his remarkable personality. Though he found himself obliged to withdraw from the Society of Friends, he retained in high degree the most admired characteristics of that community. The gentleness of his nature, his single-heartedness and companionableness endeared him to all who knew him and, as Sir Michael Sadler has said most truly, " no Indian guru had disciples more devoted, more respectful." His tastes and talents were of the widest range. In the country he was naturalist, rock-climber, and artist ; he was a much-travelled man and a good linguist. In leisure hours at home he was a gardener and a craftsman in mechanical and decorative arts and a great reader.

The character of Procter's mind was as markedly philosophical as scientific. The setting up of a " professor of leather " gave scope for a good deal of jest and indeed for some indignation in more austere academic circles. It was a constant delight to his colleagues to witness the effect of Procter's conversation in the University refectory with guests from such circles. He revelled in dialectic and could have excelled any of his colleagues in the arts of casuistry. He exercised a strong quiet influence on University affairs, most of all, perhaps, by demonstrating in himself and his work the way in which applied science may justify itself among university studies.

The establishment of the unique personal memorial of an international Research Laboratory and the bestowal of the Fellowship of the Royal Society came towards the end of Procter's life and gave him deep gratification, but he had done his work and given all his discoveries to the industry, seeking neither honours nor rewards.

A.S.

Charles Chree

# CHARLES CHREE, 1860—1928.

Dr. **Charles Chree**, the second son of the Rev. Charles Chree, D.D., was born at Lintrathen, Forfarshire, on May 5, 1860. He was educated at the Grammar School, Old Aberdeen, and at the University of Aberdeen. While at the University he did not specialise in science, but took a wide course and graduated in 1879, winning the gold medal awarded to the most distinguished graduate in arts of the year. He then went to Cambridge, where he graduated as Sixth Wrangler in 1883, being placed in the first division in Part II of the Mathematical Tripos, and in the first class in Part II of the Natural Science Tripos. He was elected to a Fellowship at King's College in 1885, which he held until he was appointed Superintendent of Kew Observatory in 1893.

During his stay in Cambridge, Chree devoted practically the whole of his time to mathematical physics. His first research, like so many more first researches of that period, was the development of a problem considered in Rayleigh's "Sound." Rayleigh had discussed the motion in a gas contained in a spherical or in a cylindrical envelope when the motion in the bounding surface is given; Chree considered certain simple forms of vibration when the solid boundary and the fluid are treated as one system. The result was presented to the Edinburgh Mathematical Society during the session 1885–86 in a paper entitled "On certain forms of Vibration." This was the first of about thirty papers written in Cambridge, mainly dealing with the mathematical theory of elasticity. Chree's contribution to the theory of elasticity alone would have given him a high place in the history of science, and it was mainly for this work that he received his F.R.S. in 1897, when his real life's work on terrestrial magnetism had hardly begun. In later life, Chree never lost his interest in this subject, and even after his removal to Kew, about fifteen papers on the subject appeared at irregular and increasing intervals. He also found his knowledge of the elasticity of solids of use to him in his later work, especially in connection with the effect of pressure on thermometers, the bending of magnetometer deflection bars, and the application of elastic solids to metrology.

While at Cambridge, Chree attended the Cavendish Laboratory and worked under J. J. Thomson. He first investigated the effect of an electric current on saturated solutions, and then experimented with liquid electrodes in vacuum tubes. This work appears to have been his only contribution to ordinary experimental physics, for after leaving Cambridge he did no further laboratory work.

Chree's skill with instruments was of a high order, but consisted chiefly in accurate and patient observations. He did not apply laboratory methods to his work at Kew, and thirty years after he had been Superintendent, the laboratory equipment at the Observatory was ludicrously inadequate. The present writer remembers with amusement the list of apparatus prepared by Chree when asked to bring his laboratory equipment up to date; it included "four rings for a retort stand" and a "nest of four beakers."

In 1893, Chree left Cambridge on his appointment to the superintendentship of the Kew Observatory. At that time Kew Observatory was controlled by a committee of the Royal Society, but it was in a very precarious financial position. The use of the Observatory and grounds, with an endowment fund of £10,000 provided by Mr. John Peter Gassiot, F.R.S., had been made over to the Royal Society in 1871. In order to eke out the meagre income from the endowment, which was not sufficient to maintain the Observatory, the testing and calibration of scientific instruments of many kinds was undertaken for suitable fees. When Chree became superintendent, the work of the Observatory consisted of three main branches. In the first place, it was the central meteorological observatory of the Meteorological Office, and maintained a constant record, by means of self-recording instruments, of all the chief meteorological elements, and in addition regular eye observations were taken at fixed hours. The second branch of work consisted in maintaining a constant record of the three components of terrestrial magnetism and of the electrical potential gradient. These again were obtained by self-recording instruments, checked and standardised by regular eye observations. The third and largest branch of the work was the verification of instruments. The magnitude of the testing work can be judged by the fact that during the ten years 1886–95 188,279 instruments of various kinds were tested. The majority of these, it is true, were clinical thermometers, but large numbers of other instruments were examined, the annual average of the chief being: thermometers other than clinical, over 3,000; watches, 744; hydrometers, 367; sextants, 348; telescopes, 273; binoculars, 257; mercury barometers, 174; aneroid barometers, 102; and a large number of other instruments, including chronometers, magnetic instruments and ordinary meteorological instruments. When Chree took over charge the work was growing, so that the actual numbers he had to deal with must have been considerably larger than the averages just mentioned, and the total staff was only fifteen.

During his first few years at Kew Chree continued to write on the theory of elasticity, but his new work soon commenced to grip him. In the year after he went to Kew he published a "Note on the Relation between the Coefficients of Pressure in Thermometry," and in the following year a "Contribution to the Theory of the Robinson Cup-anemometer." In 1895 he wrote his first paper on terrestrial magnetism, which took the form of the Report made to the Ipswich meeting of the British Association Committee on

"Comparison and Reduction of Magnetic Observations." The Report dealt with the results from the Kew magnetographs during the five years 1890–94.

In this first paper Chree announced a discovery which proved to be one of his chief contributions to the science of terrestrial magnetism and a discovery which was to tinge the whole of his future work. Chree found that if he took the mean value of the horizontal magnetic force for each hour, starting at midnight and ending at midnight, for a number of "quiet" days, the average force for the second midnight was higher than that for the first midnight, and similar results in the case of other magnetic elements. The increase in horizontal force was so great that if it continued during all days at the same rate as it did during "quiet" days the annual secular variation would be 63 times as great as the observed secular variation. Chree drew two important conclusions from this result: (*a*) that "quiet" days were not typical of ordinary days, and (*b*) that it is absolutely necessary to allow for the non-cyclic change when discussing the cyclic variation of any periodic element. In the following year he again wrote the Report of the B.A. Committee, and developed the same line of thought, using data for six years instead of five.

Chree had at last found his life's work, and from now onwards the study of terrestrial magnetism was to become his main preoccupation. It is not possible to review here in any detail the eighty odd papers, monographs, and books which contain the contributions made by Chree to the study of terrestrial magnetism and the allied subject of atmospheric electricity, but it is not difficult to outline their chief contents.

In the early years of Kew Observatory funds were not available for a complete reduction of the magnetic traces, and attention was fixed on undisturbed days. Each month the Astronomer Royal chose five days which were conspicuously quiet and, as far as possible, spaced out equally over the month. It was thought that these days would be typical of all days if the latter could be freed from the effect of disturbances which were considered to be extraneous and casual occurrences. Reference has already been made to Chree's early discovery that in one particular at least—the non-cyclic effect—they were not representative. Still, as it was then impossible to measure all days, Chree's earlier work was devoted to discussing in detail the results obtained from the quiet days, the traces of which were measured as a matter of routine. In 1903 he published in the 'Phil. Trans.' his first analysis of the results obtained from the quiet day records at Kew during the 11 years 1890 to 1900, and this was followed in the following year by a similar but less extensive analysis from the records of the Falmouth Observatory. These two papers laid the foundation of our knowledge of the normal régime of terrestrial magnetism on "quiet" days in the British Isles. It is impossible to summarize them, and it must suffice to say that they included investigations of the annual and daily variation and the relationship of magnetic phenomena to sunspots and meteorological conditions.

In 1908, Chree obtained a grant from the Government Grant Committee of the Royal Society to pay for the reduction of the traces for all days during the same 11-year period. The records thus extended were subject to the same detailed investigation, and the results discussed in three papers published in the 'Phil. Trans.' for 1908, 1910 and 1916. *It is impossible to over* estimate the importance of these five papers, for they are the only general discussion of magnetic conditions in the British Isles and they are an unfailing mine of data and information. They may be said to contain the climatology of terrestrial magnetism in the British Isles, all other papers dealing simply with magnetic weather.

That there is an intimate connection between sunspots and terrestrial magnetism had long been known. About the middle of the nineteenth century it was discovered by Sabine, Lamont and Wolf that the daily range of magnetic declination increases with an increase in the number of sunspots. In the general discussions described above, Chree had shown that a similar relationship extended also to the other magnetic elements. The relationship, however, was only of a statistical nature and the direct effect of individual sunspots on terrestrial magnetism had not been definitely demonstrated, although a number of coincidences between great solar activity and large magnetic storms had been recorded. In 1912 and 1913 Chree published in the 'Phil. Trans.' two important papers on "Some Phenomena of Sunspots and of Terrestrial Magnetism at Kew Observatory," in which he made a very successful attempt to obtain some definite information regarding the relationship which exists. between sunspots and terrestrial magnetism. Arrhenius had suggested that the magnetic disturbance effects visible on the earth are due to the discharge from the sun of electrified particles which probably take some 48 hours to travel to the earth. Chree wished to investigate this suggestion by finding the average magnetic conditions before and after the appearance of spots on the sun. For this purpose he chose the five days from each month having the largest sunspot areas as determined at Greenwich, then he tabulated the magnetic data (H range) for the fifteen days before and fifteen days after the day of large sunspot area, and found that "while in the average year there is a clear association of H ranges with sunspot area some days previously, the relation is either of a somewhat complex character, or else is liable to be much overshadowed in individual years by other influences."

Another matter which Chree investigated in these papers was the suggested tendency for magnetic storms to recur at intervals of 27 days, *i.e.*, the average period of rotation of the sun. Dr. Ad. Schmidt, of Potsdam, had stated that a large proportion of magnetic storms of the very largest kind are separated by intervals which are multiples of 29·97 days, and Mr. E. W. Maunder claimed to have demonstrated a period of 27·275 days in the magnetic storms recorded at Greenwich from 1848 to 1903. Chree, however, was not satisfied with the evidence in either case and set out to investigate the problem by an entirely different method. Instead of investigating "magnetic storms," Chree selected the five days of largest H range in each month as the point from which to start, and then by the simple method of calculating the mean magnetic character of days before and after these selected days he was able to show that the days round about 27 days after his selected disturbed day were on the average more disturbed than the average day, and that the 27th day was more highly disturbed than its neighbours. In this way Chree was able to demonstrate clearly "that if any day were considerably more disturbed than the average day of the month, then the day 27 days subsequent to it was likely to be also more disturbed than usual." In the second of the two papers on sunspots and terrestrial magnetism he carried the investigation further and showed the converse also to be true; so that the above quotation is equally true if the words "more disturbed" are replaced by "less disturbed." There can be little doubt that this demonstration of the 27-day pulse in magnetic phenomena gave Chree great pleasure and that it is amongst the best and most valuable parts of his work. Chree returned to this problem later, and the last paper of his to appear in the 'Phil. Trans.' is one on the same subject, written in conjunction with Mr. J. M. Stagg, which was published as recently as August 3, 1927.

Chree was naturally very pleased whenever a practical application could be found for the work to which he was so devoted. Underground surveying is still largely carried on by means of the magnetic needle, and to meet the wishes of the mine surveyors he commenced, in March, 1918, to publish monthly in the technical mining press the daily values of the declination at Kew and Eskdalemuir, so that the surveyors could apply corrections to their observations and discard observations taken on magnetically disturbed days. At about the same time he read a paper before the Institution of Mining Engineers on "Terrestrial Magnetism in Relation to Mine Surveying," which gave rise to an interesting discussion on the whole question of magnetic surveying in mines. One of the points brought out in the discussion was our want of knowledge of the relationship between the magnetic changes on the surface and at the bottom of a mine. A few years later an opportunity offered to investigate this point, and under the direction of Chree Mr. R. E. Watson, an assistant at Kew Observatory, established two self-recording magnetometers, one on the surface and the other in a gallery of a mine 1,800 ft. below the surface. The chief conclusion obtained from the work was that "for practical purposes, the differences between the magnetic declination changes underground and at the surface are negligible, except perhaps on days of very large disturbance."

Important as Chree's work has been on terrestrial magnetism in the British

Isles, it is questionable whether it is not surpassed in importance by his work on the magnetic conditions in the Antarctic. Chree has discussed the observations made on four expeditions to the Antarctic: (*a*) the "Southern Cross" Expedition, 1899, under Borchgrevink; (*b*) the National Antarctic Expedition, 1901–1904, under Captain R. F. Scott, R.N.; (*c*) the British Antarctic Expedition, 1910–1913, Scott's last expedition; and (*d*) the Australian Antarctic Expedition, 1911–1914, under Mawson. In addition, Chree personally trained the observers of the first three expeditions. The first expedition did not carry self-recording instruments and made only a few observations; so that Chree's discussion was not long but it was remarkably thorough. The three later expeditions used self-recording instruments and obtained records of three elements for two years in each case. In the case of Scott's two expeditions, the records were measured and reduced at Kew and Chree discussed them in addition to his normal work. In the case of Mawson's expedition, the traces were measured in Australia and Chree discussed the values supplied to him. It is necessary to examine the three volumes containing Chree's discussions of these records to realize the magnitude and importance of his work. It is true that no one else has ever had the opportunity to investigate such a mass of entirely new data; but it is impossible to imagine that anyone else could have extracted so completely the scientific information contained in such unpromising material. I welcome this opportunity of placing on record the sincere gratitude of all the magnetic observers on these expeditions to Dr. Chree for ensuring that every observation we made, often at some personal discomfort, has been put to the greatest possible use.

It has only been possible to touch on the main features of Chree's scientific work, but it must not be thought that because he devoted so much of his time to terrestrial magnetism he was at all narrow. He wrote on a number of subjects not mentioned here and he kept well abreast of the rapid developments of general physics. It is a great misfortune that Chree wrote his papers on terrestrial magnetism in a style which makes them difficult for the specialist to read and quite impossible for the average physicist. Most of his papers are discussions of the statistics derived from almost endless measurements of the magnetometer curves. These statistics had to be arranged, rearranged and compared in order to bring out different aspects of the problems under discussion. Chree himself had an uncanny facility for interpreting a line of figures without plotting them on a curve and failed to realize that other people had not this facility. In consequence, Chree's papers are illustrated by very few curves and the reader needs the greatest concentration to follow the involved text and examine the lines and columns of innumerable tables. Another trait of Chree's character which reacted on his work was his rooted objection to speculations as to the cause of the relationships he was examining. This does not mean that he was not prepared to examine and discuss the physical phenomena lying behind the relationships he found; but such speculations had to come after and separate from his statistical investigations. If only Chree could have let himself go, make hypotheses even if they were nothing more than mere guesses, and then use his statistical data to illustrate, prove or disprove his thesis, his papers would certainly have been more interesting and might have been more widely read. Chree was well aware of this side of his character and frequently went out of his way to defend it. A typical example of his defence occurs in the preface to his monograph "Studies in Terrestrial Magnetism," in which he collected together the main results of his work up to 1912:

> "The book deals almost entirely with facts, or supposed facts. The absence of a definite theory as to the origin of the several magnetic changes is due to no lack of curiosity as to the causes of things, but to a belief that at the present stage theorising is less likely to be of substantial advantage than the extension of positive knowledge. It is sometimes claimed that a theory is essential as a guide in selecting the directions in which to prosecute research. This is a partial truth. When a man devotes himself to a subject, allowing free ingress to his mind to all the ideas which the results obtained by investigators naturally suggest, he must be a very unimaginative person if profitable lines of enquiry do not force themselves on his intelligence. The difficulty is not in thinking of something to do, but of deciding what to do next. In making a choice, some may prefer the guidance supplied by a definite theory, but others will prefer to rely on their natural instinct for detecting a weak spot in the defence offered by Nature to the discovery of her secrets."

The mere volume of Chree's published work is a witness to his industry, especially when it is remembered that for the greater part of his time at Kew administrative and routine work took up a large proportion of his time. But industry went also with a high standard of criticism, and an utter want of dogmatism. When Chree, by a certain arrangement of data, had obtained the result he expected he was not satisfied until he had re-arranged his data in all possible ways and satisfied himself that each showed the effect or at least did not contradict it. Even then he was pedantically careful in stating his results and never slurred over inconvenient evidence. An example is contained in the quotation regarding the relationship between H ranges and sunspot areas which I have given above. Nine physicists out of ten would have announced this result by saying that they had "absolutely proved" clear association of H ranges with sunspot area some days previously, and on the evidence no one would have blamed them; but Chree's statement is no such confident claim, he states the weak points as well as the strong points of his results, and that was always his habit.

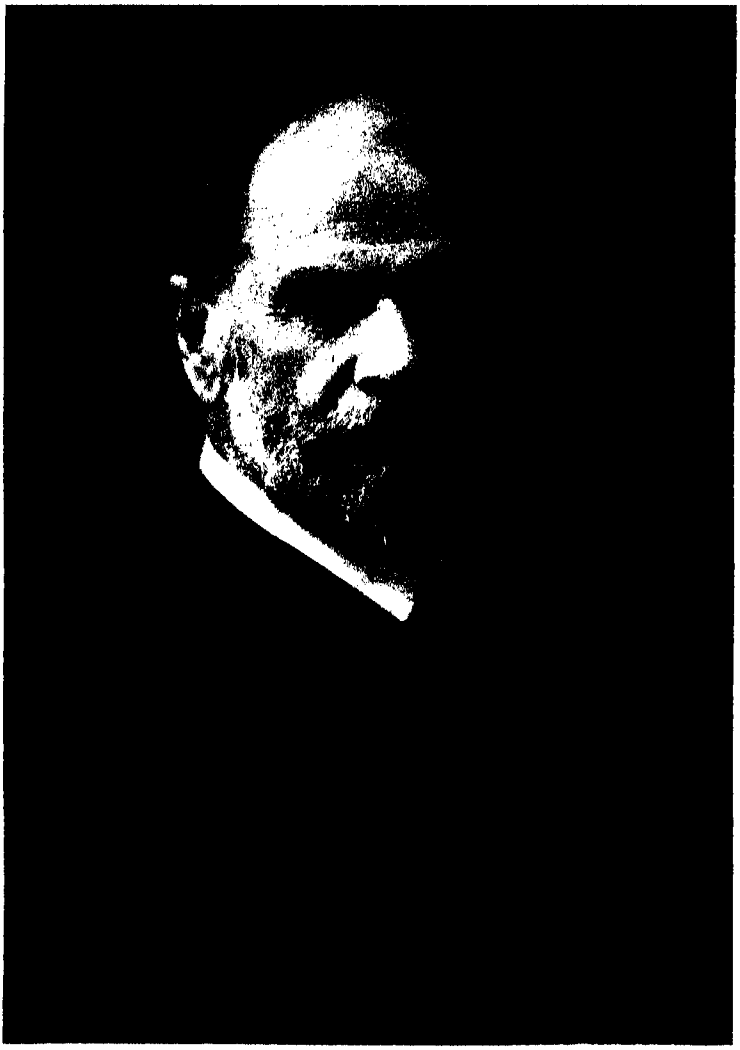
This critical habit Chree carried into all his work and no amount of trouble would deter him from re-investigating any result which did not come up to his standard; but as he expected other writers to come up to the same standard he made rather an unsatisfactory referee of papers. When given a paper to referee, Chree went through it with conscientious thoroughness, and while the author might be exasperated on receiving a long list of "remarks made by the referee," his paper could not fail to be better after he had attended to them.

Chree's nature was naturally retiring and diffident, and although he formed strong opinions, he never tried to force them on other people. He was a delightful colleague to work with, as the present writer knows from personal experience. Chree was about to graduate at Aberdeen when I was born, he taught me how to make magnetic observations; yet when in the course of time I became officially responsible for the work at Kew, Chree always consulted me and never made me feel that in comparison with him I was young and inexperienced. The same cordial spirit existed between Chree and his staff at Kew, and everyone who worked with him had a real admiration for Chree as a man and a scientist. His patience with those who went to Kew to be trained as magnetic observers was remarkable and no trouble was too great for him to take to ensure that each observer thoroughly understood the theory and practice of the magnetic instruments.

When Chree retired in 1925 under the age limit, he was in full possession of all his powers, both mental and physical, and everyone, himself included, looked forward to many years of productive scientific work, for he had much to do. He was collaborating with Mr. Stagg and was himself engaged on a discussion of the Kew records of magnetic declination from 1858 onwards and on a further discussion of Mawson's Antarctic records. He had not finished writing his paper on the magnetic declination when he was attacked by what proved to be his fatal illness, but he was able to complete this before he had to give up work early in the present year. Although he knew sometime before the end that there was no hope of recovery, he remained bright and was pleased to see his friends. The end came somewhat suddenly on August 12, when he was staying at Worthing.

Chree's degrees were Sc.D. of Cambridge and LL.D. of Aberdeen. As already stated, he was elected a Fellow of the Royal Society in 1897. He was awarded the James Watt medal by the Institution of Civil Engineers in 1905 and the Hughes medal of the Royal Society in 1919. He served as President of the Physical Society and of the Royal Meteorological Society. For a number of years Chree had the distinction of being President simultaneously of the two international organizations which deal with terrestrial magnetism. He retired from one in September, 1927, but retained the other to the time of his death.

G. C. S.



Horace Darwin

## SIR HORACE DARWIN, 1851-1928.

Sir Horace Darwin was born at Downe on May 13, 1851, the fifth son of Charles Darwin, the third of the group of brothers to become a Fellow of the Royal Society.

He was educated at Trinity College, Cambridge, taking his degree as a Senior Optime in 1874. Immediately afterwards he entered the works of Messrs. Easton and Anderson and went through the regular course of engineering in their shops, returning at the end of his apprenticeship to Cambridge. In 1877 he became an Associate Member of the Institution of Civil Engineers, and in the following year a Member of the Institution of Mechanical Engineers. The rest of his life was spent in Cambridge.

He was elected a Fellow of the Royal Society in 1903. He was a Member of the Advisory Committee for Aeronautics and delivered the first Wilbur Wright Memorial Lecture in 1913. During the war he was Chairman of the Air Inventions Committee. In 1918 he became a K.B.E. in recognition of his great services.

In 1880 he married the Hon. Emma Farrer, daughter of the first Lord Farrer, who survives him with two daughters. Their only son, Erasmus, was killed in April, 1915.

In the seventies of last century many changes were in progress in Cambridge. Recognition was being gradually given to the claims of natural science as a subject for study and research in a University, a branch of University education.

And, if at first the recognition was somewhat grudgingly bestowed, it came in time with a generous hand. New posts were created, new laboratories and workshops came into existence. Buildings known as the Museums and Lecture-rooms for some of the professors and lecturers in natural science were commenced in 1863; additions in 1877 were made to provide for comparative anatomy and physiology, while further buildings for physiology and human anatomy were erected in 1890.

Michael Foster was called to Cambridge as Trinity Prelector in Physiology in the early seventies, becoming the first Professor of the subject in 1883. Clerk Maxwell returned as Cavendish Professor of Physics in 1871, and the Cavendish Laboratory was built by the Duke of Devonshire. James Stuart became Professor of Mechanism in 1875, and engineering was recognised as a subject of University study, while medicine flourished under Sir G. M. Humphry and Sir George Paget. Liveing almost alone had kept the experimental study of chemistry alive since 1861—though there had been a

Professor since 1703, when Vigani, of Verona, was appointed; Dewar joined him as Jacksonian Professor in 1875 and new life was infused into the subject.

In the old days libraries and books, lecture rooms and class rooms were all that was required for teaching. The astronomers had their observatory, while in one or two Colleges there were small chemical laboratories, but the promotion of natural knowledge, the task of the Professors of the more modern subjects, required laboratories and their equipment, and it was in providing this that Horace Darwin found his life work.

On his return to Cambridge at Foster's request, he joined Dew Smith, and began the design and construction of scientific instruments. Foster had found that for nearly all the apparatus he required recourse to Germany was necessary. Darwin and Dew Smith, by their partnership, made a change. At first attention was paid chiefly to work for the Biological School; his rocking microphone, the outcome of an idea first put into effect by W. H. Caldwell, was perhaps the most important of his earlier products, though electrical and other physical instruments soon followed.

Work at the Cavendish Laboratory, and in particular the early experiments of Callendar on the platinum thermometer (1883) called attention to the electrical method of measuring temperature, and the need for suitable resistance boxes, galvanometers and other electrical appliances, a need further emphasised by E. H. Griffiths' work on the mechanical equivalent of heat.

After about ten years the partnership came to an end, and in 1895 the Cambridge Scientific Instrument Company was constituted with Darwin as chairman and chief shareholder. Its reputation grew apace; it was soon recognised that at Cambridge there was a firm whose instruments would bear favourable comparison with any made abroad.

In the early part of the 19th century, English instruments were admittedly pre-eminent, but toward the end of the century they had fallen far behind those of many Continental makers. Darwin changed all this, and it was realized that at the head of the new firm there was a man with a genius for design and a knowledge of mechanics which enabled him to express his design in the form most suitable for the purpose for which it was required. "Go and talk to Horace Darwin," was advice frequently given to a man seeking to devise an instrument for some delicate measurement.

His own views as to instrument design are expressed in his Wilbur Wright Lecture, delivered before the Royal Aeronautical Society in 1913, or more fully in the article which he contributed along with his colleague, Mr. C. C Mason, to the "Dictionary of Applied Physics" (vol. iii, "Instruments, The Design of Scientific").

After a discussion of the importance—in many cases the necessity—for geometric design, as laid down by Maxwell ("Handbook of Loan Collection of Instruments, 1876") and Kelvin in many of his writings, he shows by examples its advantages, though careful to point out there are cases in which it is best to disregard it. He then discusses the qualifications of the designer; he is to be a mechanical engineer with much scientific knowledge, well acquainted with the method of manufacture available, while, in order to avoid unnecessary cost, the instrument should not require great skill to make. He described himself, unwittingly, no doubt. Charles Darwin, when congratulating him on having passed some examination, had told him the art of discovering undiscovered things consists in habitually searching for the cause and necessity of everything which occurs, and that this implies sharp observance and as much knowledge as possible of the subject investigated. And this was the son's habit when asked to design an instrument; he would acquaint himself by careful observation and enquiry with all the details of the experiment or measurement to be carried out and then, when thoroughly saturated with the problem, would evolve, sometimes with great rapidity, apparatus suited for the work.

In early days he was responsible for the designs of most, if not all, of the instruments constructed by the Company, and while in later years he had the assistance of a very competent staff, his interest extended to all, though naturally in a varying degree. The booklet of "Instruments for Special Applications," issued recently, contains many which hear the impress of his skill. Among them may be mentioned the comparators, made under the supervision of Sir David Gill for the Indian Geodetic Survey, a spectroheliograph designed for the Solar Physics Observatory at Kodai Kanal, and a camera for taking star photographs, the result of a suggestion made by Prof. Turner.

Experiments on gravity always attracted him, one of his earliest instruments was a bifilar pendulum designed to detect the moon's attraction, which he developed along with his brother George; at a later date came the Cambridge half-second pendulums, now a well-known pattern, while his last work was an air-tight box in which to swing the pendulums designed for a gravity survey projected by Sir Gerald Lenox Conyngham.

And in another direction his skill was of great value to the nation. In 1909, Mr. Asquith, at the suggestion of Lord Haldane, appointed the Advisory Committee for Aeronautics for the superintendence of the investigations at the National Physical Laboratory and for general advice on the scientific problems arising in connexion with the work of the Admiralty and War Office in aerial navigation. Darwin became an active member and the trusted adviser of his colleagues on questions relating to instruments. And instruments were needed, both for work in the wind tunnels at the laboratory, and on the actual aircraft. Little was known of the forces to which an aeroplane or airship is exposed in the air; the measurement of the speed or of the direction of motion, and of the acceleration of the aircraft was no easy matter. The early pilots reported strange and mysterious stories as to the behaviour of the compass. Darwin discussed some of these in notes presented to his colleagues; he took a keen interest in the work of Keith Lucas and the production of the compass which for some time was the adopted pattern. One of the difficulties of aerial navigation was, and still is, to keep a course in a fog. Darwin devised a "turn indicator" for this purpose, which proved of value at a critical time. During the war he was an active member of various committees and, as already stated, in 1917, became Chairman of the Air Inventions Committee. His height-finder for determining the height and position of an object in the air, developed as it was by A. V. Hill and his associates, was perhaps his most important contribution to war needs, but his advice and help were continually sought and freely given.

The changes which have taken place during the last fifty years in British instruments are many and far-reaching, due to many men, but Darwin was the leader in the advance, a guide who pointed out the direction in which improvement was to be found, and a friend who freely gave of all that was in his power.

R. T. G.

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